

ELECTRON CORRELATION IN DIATOMIC MOLECULES

A thesis  
submitted in partial fulfilment  
of the requirements for the Degree  
of  
Doctor of Philosophy

by

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1977

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## 1. INTRODUCTION

This thesis investigates the use of some new techniques in obtaining approximate solutions to Schrödingers equation for diatomic molecules. The aim of this work was to develop some general methods that could be applied to any small diatomic molecule and would allow calculation of expectation values to a greater degree of accuracy than traditional methods. Throughout this work we assume the wavefunction of a diatomic molecule may be written in the form

$$\Psi = \sum_{I=1}^M a_I \psi_I \quad (1.1)$$

where the  $\psi_I$ 's are the antisymmetric product of single electron spin orbitals i.e.

$$\psi_I = \mathcal{A} \phi_1(1) \phi_2(2) \dots \phi_N(N) \quad \chi \quad (1.2)$$

The  $\phi_i$ 's are described in the confocal elliptical coordinates  $\lambda, \mu$  and  $\phi$ .

This coordinate system is the 'natural' one to choose for diatomic molecules. The one electron  $H_2^+$  molecular ion may be rigourously factored into products of the form

$$\psi = L(\lambda) M(\mu) e^{im\phi} / \sqrt{2\pi} \quad (1.3)$$

and products of this form are a convenient representation of molecular orbitals for larger molecules. For the work described in this thesis it was essential to describe the molecular spin orbitals as a product of functions of a single variable multiplied by a spin function. The form described in (1.3) was used.

With the trial wavefunction (1.1) we minimize the expectation value of the energy of the molecule with respect to independent variations of the form  $L \rightarrow L + \delta L$  and  $M \rightarrow M + \delta M$  subject to constraints of orthogonality and normalisation. This variation results in a set of coupled integro-differential equations. When the  $M$  of equation (1.1) is 1 these are the Hartree Fock (HF) equations or  $M > 1$  the multiconfiguration Hartree Fock (MCHF) equations for a diatomic molecule.

Previously the HF and MCHF equations have been solved using the methods developed by Roothaan [8] where the wavefunction is expanded in a basis set. In this work a finite difference Newton-Raphson algorithm [FDNRA] originally developed by Van Dine [12], coupled with a generalised self consistent field iteration (SCF) is used. The differential equations are translated into a set of simultaneous algebraic equations by approximating the derivatives and integrations by their finite-difference (FD) representation.

These equations are solved using FDNRA and SCF iteration. This approach has some advantages over solving the equations by expansion in a basis set.

With a basis set of  $n$  analytic functions the effort involved in solution of the problem varies as  $n^4$ . This  $n^4$  law of effort leads to slow running computer programs when a large basis set is used. A large basis set may be necessary to adequately represent a wavefunction. With a finite difference solution one does not have this  $n^4$  law of effort. Solution time is proportional to the number of mesh points, coupled with this is the fact that by solving the problem for a range of mesh spacings we may use a Richardson extrapolation [17] to estimate eigenvalues, expectation values, or any matrix element in the  $h \rightarrow 0$  limit ( $h$  = mesh spacing). No similar extrapolation technique exists for basis set solutions.

In Chapter II we consider the solution of Schrödinger's equation for  $H_2^+$ . This calculation was a trial use of the FDNRA on a molecular system. Results are presented as a series of potential energy curves for the first ten states of  $H_2^+$ .

The electronic HF equations for diatomic molecules are derived in chapter III. These are a set of coupled second-order integrodifferential equations with split boundary conditions.

Teller and Sahlin [14] have previously derived these equations for the special case of  $H_2$ , but did not solve them exactly. Aubert et al [10] have also developed a technique for approximate solution of HF equations for two electron molecules and molecular ions. These methods involve approximating the electron-electron

interaction by an analytic function in  $\lambda$  and  $\mu$ . Adjustable parameters in the potential function are either calculated from classical electrostatic theory or determined variationally. The coupled FDNRA-SCF method used by the author does not approximate the potential function by an analytic form though the assumption that it may be written in the form

$$V(\lambda, \mu, \phi) = [4/R^2 (\lambda^2 - \mu^2) [f(\lambda) + g(\lambda)]] \quad (1.4)$$

must of course be used if the HF equations are to be separable.

Generalisation of the FDNRA-SCF method to molecules with more than two electrons presents no difficulties. This may not be the case with the other methods just discussed.

Results are presented for the  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$  states of  $H_2$  and for the  $^1\Sigma_g^+$  state of  $Li_2$ . To the best of the author's knowledge, this is the first time these equations have been solved exactly.

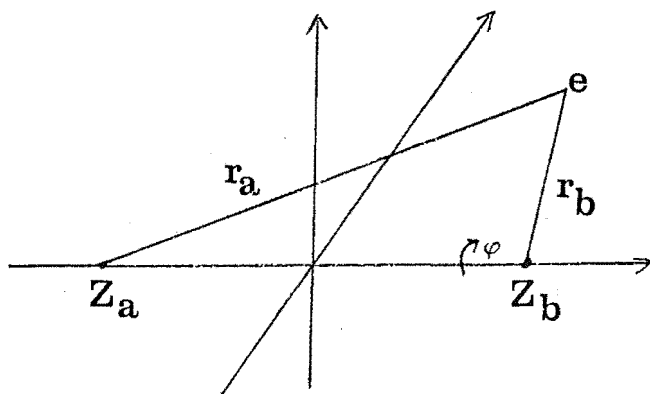
Chapter IV extends the methods developed in Chapter III to solve the MCHF equations for diatomic molecules. Many of the shortcomings of the HF method are eliminated by MCHF expansions. The total energy of  $H_2$  is very well described at nuclear separations of more than  $\approx 5$  a.u., the error in the calculated result is never more than .5% over the range of nuclear separations studied.

The bivariational equations for diatomic molecules are derived in chapter V. Here we are concerned with finding expectation values of a new operator  $C^{-1}HC$ . Here  $H$  is the normal electronic Hamiltonian of the molecule and  $C$  is a correlation function containing non-separable functions on interelectron distance. The  $C^{-1}HC$  operator has the same eigenvalue spectrum as  $H$  but does not have singularities at points where the interelectron distance approaches zero. We therefore expect to be better able to represent its eigenfunctions with smooth functions than we could for  $H$  itself. As the  $C^{-1}HC$  operator is non-Hermetian traditional variational methods are not applicable and we introduce a bivariational principle to take account of this.



## 2. SOLUTION OF $H_2^+$ TYPE SCHRÖDINGER EQUATIONS

It is well known that the two-center electronic Schrödinger equation separates in confocal elliptical coordinates  $\lambda, \mu, \phi$ . [1]



$$\lambda = (r_a + r_b) / R$$

$$\mu = (r_a - r_b) / R$$

The electronic wavefunction can be rigorously factored into the form

$$\psi = L(\lambda)M(\mu) (e^{im\phi} / \sqrt{2\pi}) \quad m = 0, \pm 1, \pm 2 \dots \quad (2.1)$$

L and M are solutions of

$$\left( \frac{d}{d\lambda} (\lambda^2 - 1) \frac{d}{d\lambda} + A - p^2 \lambda^2 + R(Z_a + Z_b) \lambda - \frac{m^2}{\lambda^2 - 1} \right) L(\lambda) = 0 \quad (2.2)$$

$$\left( \frac{d}{d\mu} (1 - \mu^2) \frac{d}{d\mu} - A + p^2 \mu^2 - R(Z_a - Z_b) \mu - \frac{m^2}{1 - \mu^2} \right) M(\mu) = 0 \quad (2.3)$$

where  $p^2 = \frac{-ER^2}{2}$  and  $A$  is a separation constant. Equations (2.2) and (2.3) are to be solved subject to the following constraints

(i) boundary conditions  $L(\infty) = 0, L(1), M(1), M(-1)$  must be finite (2.4)

(ii) normalization conditions

$$\frac{R^3}{8} \int L^2 M^2 (\lambda^2 - \mu^2) d\lambda d\mu = 1 \quad (2.5)$$

$$\int M^2 d\mu = 1 \quad (2.6)$$

Condition (2.6) is required to uniquely determine  $L$  and  $M$  since a transformation of the form  $L' = \alpha L, M' = M/\alpha$  leaves (2.5) unaltered. For  $m \neq 0$  equation (2.2) has a singularity at  $\lambda=1$  and equation (2.3) has a singularity at  $\mu = \pm 1$ . Substitution of the forms

$$L(\lambda) = (\lambda^2 - 1)^{m/2} L'(\lambda) \quad (2.7)$$

$$M(\mu) = (1 - \mu^2)^{m/2} M'(\mu)$$

removes these singularities. Equations (2.2) and (2.3) become

$$[(\lambda^2 - 1) \frac{d^2}{d\lambda^2} + 2(m+1) \lambda \frac{d}{d\lambda} + A + m(m+1) + R\lambda(Z_a + Z_b)] L'(\lambda) = 0 \quad (2.8)$$

$$\begin{aligned}
& [(1-\mu^2) \frac{d^2}{d\mu^2} + 2(m+1)\mu \frac{d}{d\mu} - A + m(m+1) - R\mu(Z_a - Z_b) \\
& + p^2\mu^2]M'(\mu) = 0
\end{aligned} \tag{2.9}$$

It is convenient from a computational viewpoint to further transform (2.8) and (2.9)

$$X = (\lambda^2 - 1)L' \tag{2.10}$$

$$Y = (1 - \mu^2)M' \tag{2.11}$$

$$\zeta = (\lambda - 1)/(c\lambda - c + 1) \quad c > 0 \quad 0 \leq \zeta \leq 1/c \tag{2.12}$$

$$\rho = \mu/(a - \mu^2) \quad a > 1 \quad -1/(a-1) \leq \rho \leq 1/(a-1) \tag{2.13}$$

since zero boundary conditions are easier to apply than nonsingular boundary conditions. The need for these transformations will become apparant later in the chapter when the finite difference form of equations (2.8) and (2.9) is presented.

In terms of the  $\zeta$  and  $\rho$  independent variables equations (2.8) and (2.9) become:

$$\begin{aligned}
& [(2\zeta + (1-2c)\zeta^2)(1-c\zeta)^2 \frac{d^2}{d\zeta^2} \\
& + (2(m-1)(1+(1-c)\zeta)(1-c\zeta) - 2c(2\zeta + (1-2c)\zeta^2)(1-c\zeta)) \frac{d}{d\zeta} \\
& + \frac{2(2+(2-4c)\zeta + (1-2c+2c^2)\zeta^2) - 4m(1+(1-c)\zeta)(1-c\zeta)}{(2\zeta + (1-2c)\zeta^2)}
\end{aligned}$$

$$+ A + m(m+1) - \frac{p^2(1+(1-c)\zeta)^2}{(1-c\zeta)^2} + \frac{2R(1+(1-c)\zeta)}{1-c\zeta}]X(\zeta) = 0 \quad (2.14a)$$

and

$$\begin{aligned} & \left[ \frac{\rho^2(1+4a\rho^2)(4\rho^2 - (\sqrt{1+4a\rho^2} - 1)^2)}{(\sqrt{1+4a\rho^2} - 1)^2} \frac{d^2}{d\rho^2} \right. \\ & + \left( \frac{2\rho(4\rho^2 - (\sqrt{1+4a\rho^2} - 1)^2)(\sqrt{1+4a\rho^2} - (1+6a\rho^2))}{(\sqrt{1+4a\rho^2} - 1)^3} \right. \\ & \left. \left. - 2(m-1)\rho\sqrt{1+4a\rho^2} \right) \frac{d}{d\rho} \right. \\ & + \frac{2(4\rho^2 + (\sqrt{1+4a\rho^2} - 1)^2) - 8m\rho(\sqrt{1+4a\rho^2} - 1)}{4\rho^2 - (\sqrt{1+4a\rho^2} - 1)^2} \\ & \left. + \frac{p^2(\sqrt{1+4a\rho^2} - 1)^2}{8\rho^2} - A - m(m+1) \right] Y(\rho) = 0. \quad (2.15a) \end{aligned}$$

Expressing (2.14) and (2.15) more concisely we have:

$$\begin{aligned} & [B(\zeta) \frac{d^2}{d\zeta^2} + C(\zeta) \frac{d}{d\zeta} + D(\zeta) + A - \frac{p^2(1+(1-c)\zeta)^2}{(1-c\zeta)^2}] \\ & \cdot X(\zeta) = 0 \quad (2.14b) \end{aligned}$$

and

$$\begin{aligned} & [B'(\rho) \frac{d^2}{d\rho^2} + C'(\rho) \frac{d}{d\rho} + D'(\rho) - A + \frac{p^2(\sqrt{1+4a\rho^2} - 1)}{8\rho^2}] \\ & \cdot Y(\rho) = 0. \quad (2.15b) \end{aligned}$$

The normalisation conditions became:

$$\begin{aligned}
 & \frac{R^3}{8} \int X^2 Y^2 \left[ \frac{(1-c\zeta)^2}{2\zeta + (1-2c)\zeta^2} \right]^{(2-m)} \cdot \left[ \frac{4\rho^2}{4\rho^2 - (\sqrt{1+4a\rho^2} - 1)^2} \right]^{(2-m)} \\
 & \cdot \frac{1}{(1-c\zeta)^2} \cdot \frac{(\sqrt{1+4a\rho^2} - 1)}{2\rho^2 \sqrt{1+4a\rho^2}} \cdot \left( \left[ \frac{1+(1-c)\zeta}{1-c\zeta} \right]^2 - \left[ \frac{-1+\sqrt{1+4a\rho^2}}{\rho} \right]^2 \right) \\
 & \cdot d\rho d\zeta - 1 = 0
 \end{aligned} \tag{2.16}$$

and

$$\int Y^2 \left[ \frac{4\rho^2}{4\rho^2 - (\sqrt{1+4a\rho^2} - 1)^2} \right]^{(2-m)} \frac{(\sqrt{1+4a\rho^2} - 1)}{2\rho^2 \sqrt{1+4a\rho^2}} d\rho - 1 = 0. \tag{2.17}$$

The equations (2.14) through (2.17) are now translated into finite difference form. The  $\zeta$  axis is divided into  $N_1-1$  equally spaced mesh points and the  $\rho$  axis into  $N_2-1$  equally spaced mesh points.

Derivatives in (2.14b) and (2.15b) are approximated by

$$\left. \frac{dX}{d\zeta} \right|_{\zeta_k} = \frac{1}{2h_1} (X_{k+1} - X_{k-1}) + O(h_1^2) \tag{2.18}$$

$$\left. \frac{d^2X}{d\zeta^2} \right|_{\zeta_k} = 1/h_1^2 (X_{k+1} - 2X_k + X_{k-1}) + O(h_1^2) \tag{2.19}$$

where  $h_1 = 1/c/N_1$ ,  $h_2 = 2/(a-1)/N_2$

$$\zeta_k = kh_1, \quad k = 0, 1 \dots N_1 \tag{2.20}$$

$$X_k = X(\zeta_k)$$

$$\rho_k = -1/(a-1) + kh_2$$

$$Y_k = Y(\rho_k) \quad (2.20)$$

derivatives of  $Y$  are similarly approximated.

Using these approximations equations (2.14) and (2.15) may be written as a system of  $N_1 + N_2 - 2$  algebraic equations, the unknowns being the values of  $X_k$  and  $Y_k$  at the internal mesh points and the eigenvalues  $\rho^2$  and  $A$ . The integrals (2.16) and (2.17) are approximated by trapazoidal rule summations. This is consistent with the  $O(h^2)$  error in the approximations to the derivatives. In finite difference form equation (2.14) becomes at mesh point  $k$

$$\begin{aligned} & \frac{k(2+(1-2c)kh_1)(1-ckh_1)^2}{h_1} (X_{k+1} + X_{k-1}) + \\ & \left[ \frac{(m-1)(1+(1-c)kh_1)(1-ckh_1) - c(2kh_1 + (1-2c)k^2h_1^2)(1-ckh_1)}{h_1} \right] \\ & (X_{k+1} - X_{k-1}) + \\ & \left[ - \frac{2k(2+(1-2c)kh_1)(1-ckh_1)^2}{h_1} + A + m(m+1) + \right. \\ & \left. \frac{p^2(1+(1-c)kh_1)}{2(1-ckh_1)^2} \right] X_k = 0 \end{aligned} \quad (2.21)$$

We may also write equation (2.16) in terms of mesh point number, however this leads to very complex expressions and conceals the form of the equation.

Therefore we write this equation in a simpler form than (2.21).

$$\begin{aligned}
 & \frac{\rho_k^2 s_k (4\rho_k^2 - (s_k^{\frac{1}{2}} - 1)^2)}{(s_k^{\frac{1}{2}} - 1) h_2^2} (Y_{k+1} + Y_{k-1}) \\
 & + \frac{2\rho_k (4\rho_k^2 - (s_k^{\frac{1}{2}} - 1)^2) (s_k^{\frac{3}{2}} - (1+6a\rho_k^2))}{(s_k^{\frac{1}{2}} - 1)^3 h_2} \\
 & - \frac{2(m-1)\rho_k s_k^{\frac{1}{2}}}{h_2} (Y_{k+1} - Y_{k-1}) \\
 & + \left[ -\frac{2\rho_k^2 s_k (4\rho_k^2 - (s_k^{\frac{1}{2}} - 1)^2)}{(s_k^{\frac{1}{2}} - 1) h_2} - \frac{p(s_k^{\frac{1}{2}} - 1)^2}{8\rho_k^2} \right. \\
 & \left. + \frac{2(4\rho_k^2 + (s_k^{\frac{1}{2}} - 1)^2) - 8m\rho_k (s_k^{\frac{1}{2}} - 1)}{4\rho_k^2 - (s_k^{\frac{1}{2}} - 1)^2} - A - m(m+1) \right] Y_k \\
 & = 0
 \end{aligned} \tag{2.22}$$

where  $s_k = (1+4a\rho_k^2)$

and  $\rho_k = -1/(a-1) + kh_2$ .

Similarly the normalisation equations (2.15), (2.16) become

$$\sum_{k=1}^{N_1-1} x_k^2 \left[ \frac{(1-ckh_1)^2}{2kh_1 + (1-2c)k^2 h_1^2} \right]^{(2-m)} \frac{(1+(1-c)kh_1)^2}{(1-ckh_1)^4} .$$

$$\begin{aligned}
& \sum_{\ell=1}^{N_2-1} Y_{\ell}^2 \left[ \frac{4\rho_{\ell}^2}{4\rho_{\ell}^2 + (s_{\ell}^{\frac{1}{2}}-1)^2} \right]^{(2-m)} \frac{(s_{\ell}^{\frac{1}{2}}-1)}{2\rho_{\ell}^2 s_{\ell}^{\frac{1}{2}}} - \\
& \sum_{k=1}^{N_1-1} X_k^2 \left[ \frac{(1-ckh_1)^2}{2kh_1 + (1-2c)k^2 h_1^2} \right]^{(2-m)} \frac{1}{(1-ckh_1)^2} \cdot \\
& \sum_{\ell=1}^{N_2-1} Y_{\ell}^2 \left[ \frac{4\rho_{\ell}^2}{4\rho_{\ell}^2 + (s_{\ell}^{\frac{1}{2}}-1)^2} \right]^{(2-m)} \frac{(s_{\ell}^{\frac{1}{2}}-1)}{2\rho_{\ell}^2 s_{\ell}^{\frac{1}{2}}} \cdot \left( \frac{-1+s_{\ell}^{\frac{1}{2}}}{\rho_{\ell}} \right)^2 \\
& = 8/(R^3 h_1 h_2) \tag{2.23}
\end{aligned}$$

and

$$\sum_{\ell=1}^{N_2-1} Y_{\ell}^2 \left[ \frac{4\rho_{\ell}^2}{4\rho_{\ell}^2 - (s_{\ell}^{\frac{1}{2}}-1)^2} \right]^{(2-m)} \frac{(s_{\ell}^{\frac{1}{2}}-1)}{2\rho_{\ell}^2 s_{\ell}^{\frac{1}{2}}} = 1/h_2 \tag{2.24}$$

Equations (2.23) and (2.24) are only correct if the integrands go to zero at the endpoints of the integral. This in fact does not happen and endpoint corrections too complex to be written here must be included to make (2.23) and (2.24) strictly correct. How this is done is covered in appendix D.

We now have  $N_1+N_2$  algebraic equations in the unknowns,  $X_k$ , ( $k = 1 \dots, N_1-1$ ),  $Y_k$ , ( $k = 1 \dots, N_2-1$ ),  $A$  and  $p^2$ . The values of  $X_0, X_{N_1}, Y_0, Y_{N_2}$  are known explicitly to be zero from the boundary conditions (2.4). We now see that the transformations (2.10) and (2.11) have made the physical boundary conditions very easy to apply in terms of the finite difference variables.



NEWTON-RAPHSON ALGORITHM

The Newton-Raphson method for the solution of systems of non-linear equations is well known, so I will just give a brief outline of the method. For a more complete derivation of the method see, for example, [15].

Consider a set of nonlinear algebraic equations

$$f_k(z_1, z_2 \dots z_N) = 0 \quad k = 1, \dots, N. \quad (2.25)$$

Let  $\zeta_1, \zeta_2 \dots \zeta_k$  be a solution of (2.25). Expanding the  $f_k$ 's about the point  $\bar{z}_k^i$  where the  $z_k^i$  ( $k = 1 \dots N$ ) constitute an approximate solution to the  $\zeta_k$  ( $k = 1 \dots N$ ) we have,

$$0 = f_k(\bar{\zeta}) = f_k(\bar{z}^i) + \sum_{j=1}^N \left. \frac{\partial f_k}{\partial z_j} \right|_{z_j^i} (\zeta_j - z_j^i) + \dots \quad (2.26)$$

$$k = 1, \dots, N$$

or rearranging,

$$\sum_j \left. \frac{\partial f_k}{\partial z_j} \right|_{z_j^i} (\zeta_j - z_j^i) = -f_k(\bar{z}^i) + \sum_j O(\zeta_j - z_j^i)^2 \quad (2.27)$$

$$k = 1 \dots N.$$

Neglecting higher order terms this can be written in the matrix form

$$J (\bar{\zeta} - \bar{z}^i) \approx -\bar{F}$$

where  $J$  is the  $N \times N$  matrix

$$J_{kj} = \frac{\partial f_k}{\partial z_j}$$

or

$$\bar{\zeta} \approx \bar{z}^i - J^{-1} \bar{F} \quad (2.28)$$

Thus to solve (2.25) we iterate using (2.28) to define new approximations to  $\bar{\zeta}$  until  $\max (|F_1|, |F_2| \dots |F_N|) <$  a given tolerance. We call this procedure a generalized Newton-Raphson iteration (GNRI).

The application of the GNRI to the system (2.21)-(2.24) is best understood if we make a small change in notation at this point. We represent all the unknowns by a single vector  $\bar{P}$ .  $\bar{P}$  is defined as follows,

$$\begin{aligned} P_k &= X_k, \quad k = 1 \dots N_1-1, \\ P_{k+N_1-1} &= Y_k, \quad k = 1 \dots N_2-1, \\ P_{N_1+N_2-1} &= p^2, \\ P_{N_1+N_2} &= A. \end{aligned} \quad (2.29)$$

Equations (2.21) - (2.24) when written in terms of the  $P_k$ 's comprise a system of the form,

$$f_k(P_1, P_2 \dots P_{N_1+N_2}) = 0, \quad k = 1, 2, \dots, N_1+N_2,$$

where

$$f_k = B(\zeta_k)(P_{k+1} - 2P_k + P_{k-1})/h_1^2 + C(\zeta_k)(P_{k+1} - P_{k-1})/2h_1 \\ + D(\zeta_k)P_k \frac{P_{N_1+N_2-1}(1+(1-C)\zeta_k)^2}{(1-C\zeta_k)^2} P_k = 0 \quad k = 1, 2 \dots N_1-1, \quad (2.30)$$

$$f_k = B'(\rho_\ell)(P_{k+1} - 2P_k + P_{k-1})/h_2^2 + C'(\rho_\ell)(P_{k+1} - P_{k-1})/2h_2 \\ + D(\rho_\ell)P_k^{-P_{N_1+N_2-1}} \frac{(\sqrt{1+4a\rho_\ell^2}-1)}{8\rho_\ell^2} = 0 \quad k=N_1, N_1+1, \dots, N_1+N_2-2 \quad (2.31)$$

where  $\rho_\ell = \rho_{k-N_1+1}$ .

Normalisation equations (2.23) and (2.24) may also be written in terms of the  $P_k$ 's,

$$f_{N_1+N_2-1} = \sum_{i=1}^{N_1} P_i^2 \left[ \frac{(1-ci h_1)^2}{2i h_1 + (1-2c)i^2 h_1^2} \right]^{(2-m)} \frac{(1+(1-c)ih_1)}{(1-ci h_1)^4}.$$

$$\sum_{\ell=1}^{N_1} P_{\ell+N_1-1}^2 \left[ \frac{4\rho_\ell^2}{4\rho_\ell^2 + (s_\ell^{\frac{1}{2}}-1)^2} \right]^{(2-m)} \frac{(s_\ell^{\frac{1}{2}}-1)}{2\rho_\ell^2 s_\ell^{\frac{1}{2}}} -$$

$$\sum_{i=1}^{N_1} P_i^2 \left[ \frac{(1-ci h_1)^2}{2i h_1 + (1-2c)i^2 h_1^2} \right]^{(2-m)} \frac{1}{(1-ci h_1)^2}.$$

$$\sum_{\ell=1}^{N_2} P_{\ell+N_1-1}^2 \left[ \frac{4\rho_\ell^2}{4\rho_\ell^2 + (s_\ell^{\frac{1}{2}}-1)^2} \right]^{(2-m)} \frac{(s_\ell^{\frac{1}{2}}-1)}{2\rho_\ell^2 s_\ell^{\frac{1}{2}}} \left( \frac{-1+s_\ell^{\frac{1}{2}}}{\rho_\ell} \right)^2$$

$$- 8/(P_1^3 h_1 h_2) \quad (2.32)$$

and

$$f_{N_1+N_2} = \sum_{\ell} P_{\ell+N_1-1}^2 \left[ \frac{4\rho_{\ell}^2}{4\rho_{\ell}^2 - (s_{\ell}^{\frac{1}{2}}-1)^2} \right]^{(2-m)} \frac{(s_{\ell}^{\frac{1}{2}}-1)}{2\rho_{\ell}^2 s_{\ell}^{\frac{1}{2}}} - 1 \quad (2.33)$$

These equations are now in a form suitable for solution using GNRI.

It remains only to define an initial approximation to the solution vector  $P_k$   $k = 1, \dots, N_1+N_2$ . The procedure adopted was to use atomic hydrogenic wavefunctions expressed in confocal elliptic coordinates at a small value of nuclear separation ( $R \approx .3$  a.u.). Once a converged solution for a given value of  $R$  is obtained, this may be used as a starting solution for larger values of  $R$ . Thus we may 'track' on nuclear separation and obtain wavefunctions and eigenvalues for a large range of  $R$ . The molecular state converged upon depends of course on the hydrogenic state used as a starting approximation. Because of the special nature of the Jacobian matrix of equations (2.21) - (2.24) a rapid method of inversion may be used [16]. This is described in appendix A.

## RESULTS OF CALCULATIONS

The principal reason for doing calculations on  $H_2^+$  is that since analytic solutions exist it enables us to check the accuracy available using finite difference methods. A further reason is that through the one electron

case we can generate starting approximations for orbitals of larger diatomic molecules.

For any finite values of  $h_1$  and  $h_2$  we have only an approximate solution to Schrödinger's equation. However by solving (2.21) - (2.24) for a range of mesh spacings we may then perform a Richardson Extrapolation [17] to the  $h \rightarrow 0$  limit. As an example of this procedure and to demonstrate the accuracy available using finite difference methods a Neville table of a Richardson extrapolation is presented in Table [2.1]. Here the energy of the  $2p\pi_u$  state for  $R = 3$  a.u. has been extrapolated to give agreement with analytic methods to seven decimal places. By increasing the number of terms in the extrapolation this agreement can be further improved. Also presented are graphs of density of points along the internuclear axis for different values of  $a$  and  $c$  in the transformations (2.12) and (2.13). These transformations have the following advantages. The range of the  $\zeta$  variable is finite and thus can be spanned by a finite number of points, it also gives a greater density of points in  $\lambda$  space for  $\lambda \rightarrow 1$  than it does for large  $\lambda$ . The spacing of these points can be varied by varying  $c$  in (2.12). For a  $1\sigma_g$  state we choose a value of  $c$  giving a high density of points near  $\lambda=1$  while for a  $3\sigma_g$  state a value of  $c$  giving high density of points for larger  $\lambda$  is chosen. While this is not essential for accurate results, it does reduce the number of different mesh spacings required for a reliable extrapolation.

The  $\rho$  transformation (2.13) performs a similar function, it enables us to vary the density of points about  $\mu = \pm 1$ . It is of most value in  $H_2^+$  calculations for internuclear separations greater than about 10 a.u. or equivalently  $(Z_a + Z_b) R \geq 20$  for other nuclear ions.

In Table 2.2 we investigate a generalisation of the Richardson Extrapolation. Here the dependance on  $h_1$  and  $h_2$  is considered separately. We assume that the energy (or separation constant) is a continuous function of  $h_1$  and  $h_2$ , expanding it in a Taylor series about the point  $h_1 = h_2 = 0$  gives,

$$E(h_1, h_2) = a_1 + a_2 h_1^2 + a_3 h_2^2 + a_4 h_1^4 + a_5 h_2^4 + \\ a_6 h_1^2 h_2^2 + a_7 h_1^6 + a_8 h_2^6 + a_9 h_1^2 h_2^4 + a_{10} h_1^4 h_2^2 + \dots \quad (2.34)$$

Odd powers of  $h_1$  and  $h_2$  need not be included in the expansion since inverting the coordinate system ( $h_1 \rightarrow -h_1$ ), ( $h_2 \rightarrow -h_2$ ) must leave  $E$  unchanged. By calculating  $E$  for a range of  $h_1$  and  $h_2$  we may use (2.34) to extrapolate the results. The procedure is fully described in [44].

This procedure may be simplified by writing  $h_2 = \alpha h_1$ , (2.34) then becomes

$$E(h_1, h_2) = a_1 + a_2^1 h_1^2 + a_4^1 h_1^4 + a_6^1 h_1^6 + \dots$$

So providing the ratio  $h_1/h_2 = \alpha$  is constant for the range of mesh spacings to be used for an extrapolation then the complexities introduced by (2.34) need not be considered and a simple Richardson's Extrapolation can be used. This was the procedure adopted for most of the work described in this thesis.

Table 2.1: Neville Table for the Energy of the  $2p\pi_u$   
State of  $H_2^+$  at  $R = 3AU$

$N_1=N_2$

80	.386480067	.386443851	
100	.386470965	.386443852	.386443852
120	.386464650		

Table 2.2: Generalized Neville Table for the Energy of the  
 $1s\sigma_g$  state of  $H_2^+$  at  $R = 2$  AU.

$h_1$	$h_2$	Zeroth Order Extrapolant	First Order Extrapolant	2nd Order Extrapolant	3rd Order Extrapolant
0.01234568	0.02469136	-1.1026582			
0.01234568	0.01652893	-1.1034901	-1.1024967		
0.00826446	0.02469136	-1.1017924	-1.1028660		
				-1.1026218	
0.01234568	0.01242236	-1.1038203	-1.1024840		
				-1.1026213	
0.00621118	0.02469136	-1.1014599	-1.1025791		-1.1026276
				-1.1026213	
0.00826446	0.01652893	-1.1026227	-1.1025312		-1.1026276
				-1.1026214	
0.00621118	0.01652893	-1.1022897	-1.1026149		
				-1.1026287	
0.00826446	0.01242236	-1.1029524	-1.1026146		
				-1.1026264	
0.00684932	0.01315789	-1.1026534	-1.1026212		
0.00662252	0.01282051	-1.1026509	-1.1026217		
0.00621118	0.01242236	-1.1026191			



### Potential Energy of $\text{H}_2^+$ (Fig 2.1)

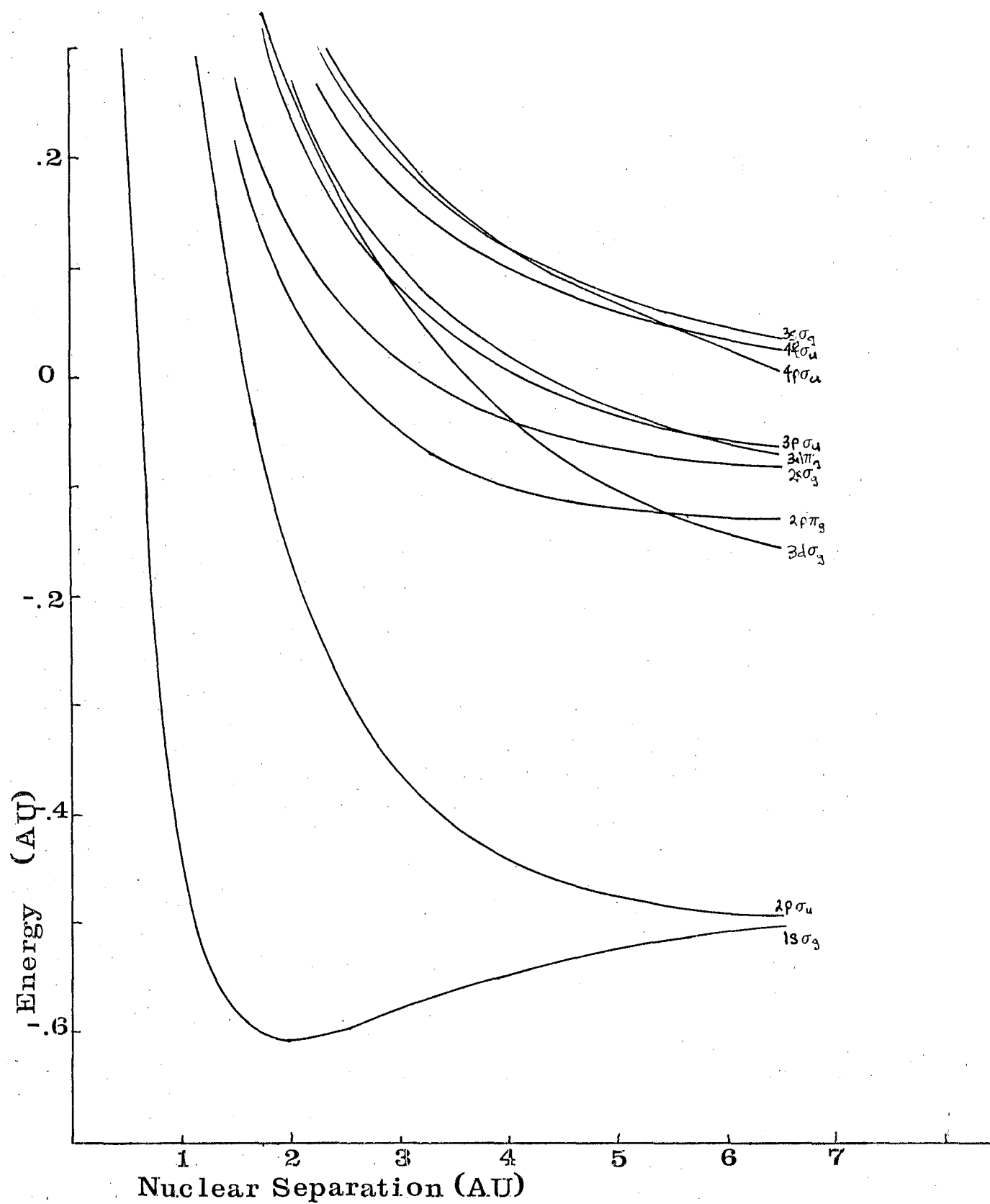
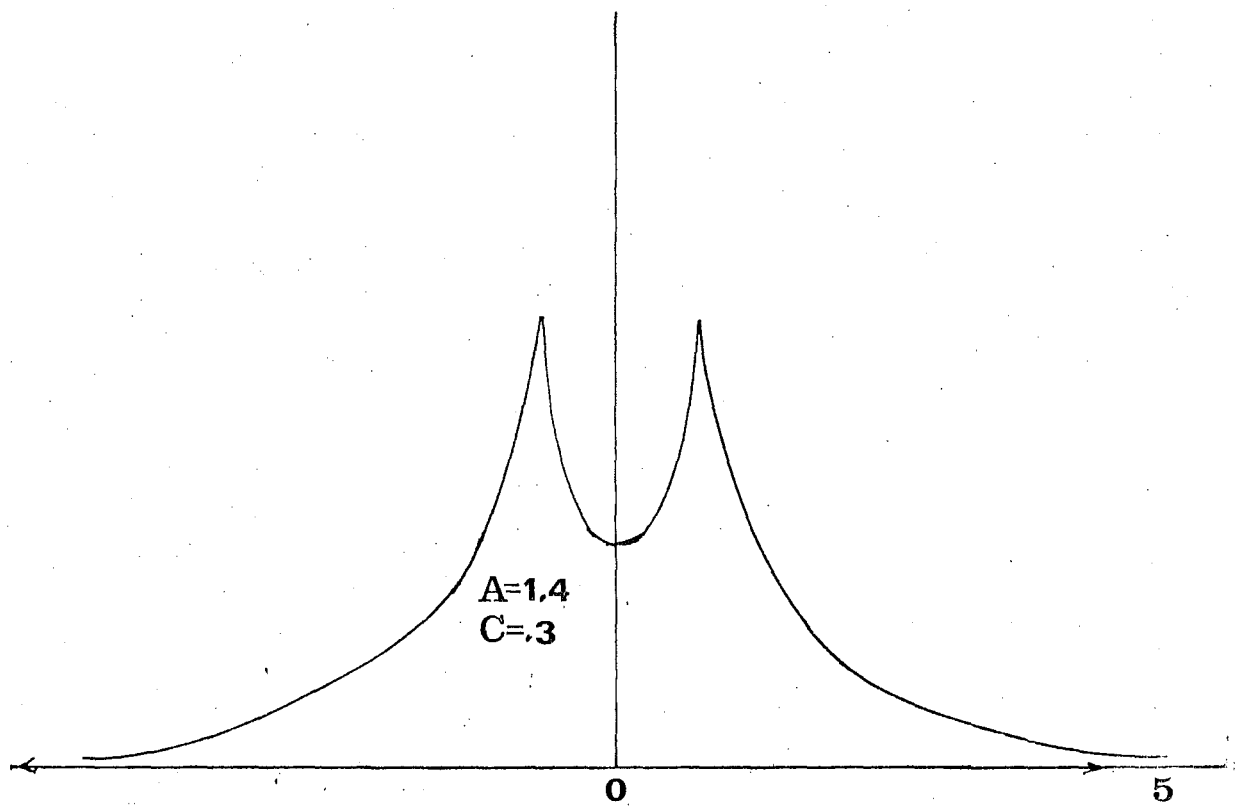
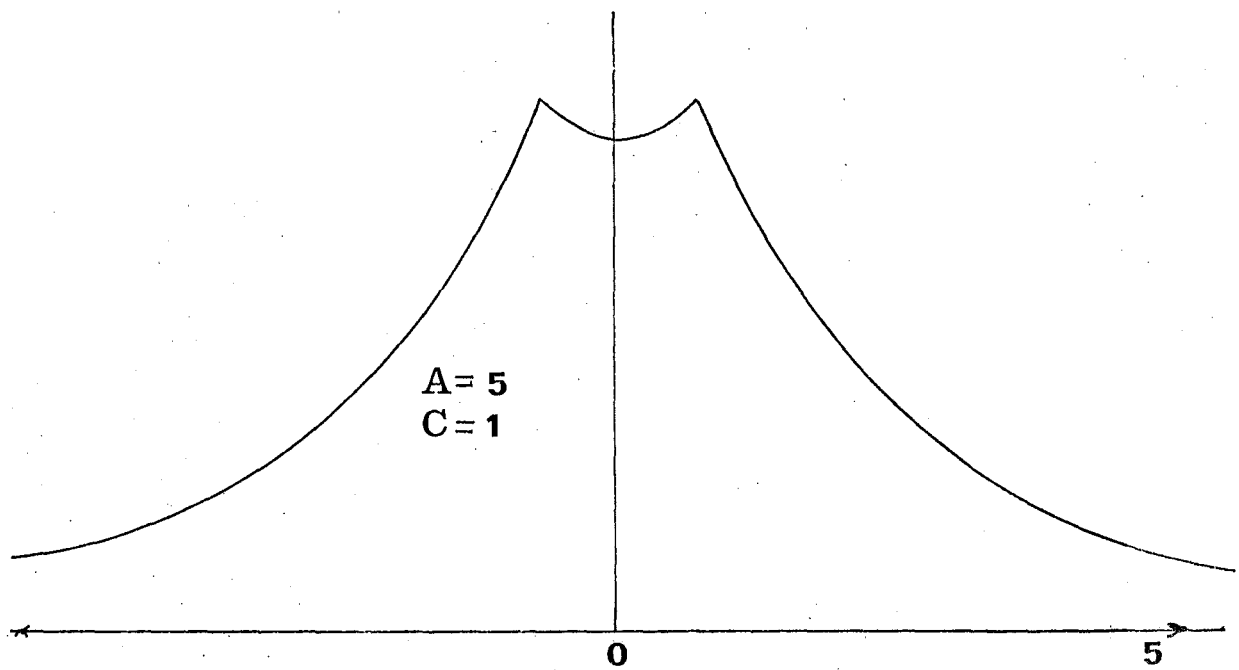


Fig 2.2  
Density of FD Grid



### 3. THE HARTREE-FOCK EQUATIONS FOR DIATOMIC MOLECULES

#### GENERAL

It is assumed that the electronic wavefunction for a diatomic molecule may be factored into the form

$$\psi = \mathcal{A} \phi_1(1) \phi_2(2) \dots \phi_N(N) \quad (3.1)$$

where

$$\phi_\alpha(\alpha) = L_\alpha(\lambda_\alpha) M_\alpha(\mu_\alpha) \frac{e^{im_\alpha \phi_\alpha}}{\sqrt{2\pi}} \chi_{\frac{1}{2}}^{m_{s_\alpha}} \quad .$$

$\lambda, \mu$  and  $\phi$  are the usual confocal elliptic coordinates and  $\chi_{\frac{1}{2}}^{m_{s_\alpha}}$  represents the spinors  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$  and  $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$  for  $m_{s_\alpha} = \pm \frac{1}{2}$  respectively.

By minimizing the expectation value of the Hamiltonian with respect to independent variations in  $L_\alpha$  and  $M_\alpha$ ,  $\alpha = 1, \dots, N$ , subject to normalisation and orthogonality constraints, a set of coupled integrodifferential equations for the  $L_\alpha$  and  $M_\alpha$  results. These equations have been derived for the specific case of  $H_2$  by Teller and Sahlin [14], and an approximate solution given. More recently Aubert, Bessis and Bessis [19] have developed another method to calculate approximate solutions to these equations in the two electron case.

In the present work the FDNRA [16] is used, coupled with a more general approach to the self consistent field (SCF) iteration to obtain numerical solutions to these equations.

The electronic Hamiltonian for a N electron diatomic molecule with nuclear charges  $Z_a$  and  $Z_b$  separated by a distance R is, in atomic units,

$$H = \sum_i \left( -\frac{1}{2} \nabla_i^2 - \left( \frac{Z_a}{r_{ia}} + \frac{Z_b}{r_{ib}} \right) + \frac{1}{2} \sum_{j \neq i} \frac{1}{r_{ij}} \right) \quad (3.2)$$

Assuming the form (3.1) as a trial solution to Schrödinger's equation we form the functional

$$\Theta = \langle \psi | H | \psi \rangle - \sum_{\alpha\beta} \epsilon_{\alpha\beta} \langle \phi_i | \phi_j \rangle, \quad (3.3)$$

where  $\epsilon_{\alpha\beta}$  are a set of Lagrange multipliers on orthogonality and normalisation.

By demanding  $\delta\Theta$  be zero with respect to independent variations  $L \rightarrow L + \delta L$  and  $M \rightarrow M + \delta M$  we arrive at one form of the HF equations for a diatomic molecule.

$$\begin{aligned} & \left[ \frac{d}{d\lambda} (\lambda^2 - 1) \frac{d}{d\lambda} - \frac{m_\alpha^2}{\lambda^2 - 1} + R(Z_a + Z_b)\lambda + A_{1\alpha} - B_\alpha(\lambda) + p_{\alpha\alpha}^2 \lambda^2 \right] L_\alpha(\lambda) \\ & + C_\alpha(\lambda) + \sum_{\beta \neq \alpha} D_{\alpha\beta}(\lambda) \epsilon_{\alpha\beta} L_\beta(\lambda) = 0 \quad \alpha = 1, N \end{aligned} \quad (3.4a)$$

$$\begin{aligned} & \left[ \frac{d}{d\mu} (1 - \mu^2) \frac{d}{d\mu} - \frac{m_\alpha^2}{1 - \mu^2} - R(Z_a - Z_b)\mu - A_{2\alpha} - G_\alpha(\mu) - p_{\alpha\alpha}^2 \mu^2 \right] M_\alpha(\mu) \\ & + H_\alpha(\mu) + \sum_{\beta \neq \alpha} E_{\alpha\beta}(\mu) \epsilon_{\alpha\beta} M_\beta(\mu) = 0 \quad \alpha = 1, N \end{aligned} \quad (3.4b)$$

where

$$\begin{aligned} D_{\alpha\beta}(\lambda) &= \Delta(\alpha, \beta) \left[ \lambda^2 \int_{-1}^{+1} M_\alpha(\mu) M_\beta(\mu) d\mu - \int_{-1}^{+1} \mu^2 M_\alpha(\mu) M_\beta(\mu) \mu^2 d\mu \right] \\ E_{\alpha\beta}(\mu) &= \Delta(\alpha, \beta) \left[ \int_{-1}^{+1} L_\alpha(\lambda) L_\beta(\lambda) \lambda^2 d\lambda - \mu^2 \int_{-1}^{+1} L_\alpha(\lambda) L_\beta(\lambda) d\lambda \right] / \int_{-1}^{+1} L_\alpha^2(\lambda) d\lambda \end{aligned}$$

$$\Delta(\alpha\beta) = \delta(m_\alpha m_\beta) \delta(m_{s\alpha} m_{s\beta})$$

The constants  $A_{1\alpha}$  and  $A_{2\alpha}$  in (3.4a) and (3.4b) are defined by

$$A_{1\alpha} = \frac{\int_{-1}^{+1} M_{\alpha}(\mu) \left[ \frac{d}{d\mu} (1-\mu^2) \frac{d}{d\mu} - \frac{m_{\alpha}^2}{1-\mu^2} + R(Z_A - Z_B) \mu - p_{\alpha\alpha}^2 \mu^2 \right] M_{\alpha}(\mu) d\mu}{\int M_{\alpha}^2(\mu) d\mu}$$

$$A_{2\alpha} = \frac{- \int L_{\alpha}(\lambda) \left[ \frac{d}{d\lambda} (\lambda^2 - 1) \frac{d}{d\lambda} - \frac{m_{\alpha}^2}{\lambda^2 - 1} + R(Z_a + Z_b) \lambda + p_{\alpha\alpha}^2 \lambda^2 \right] L_{\alpha}(\lambda) d\lambda}{\int L_{\alpha}^2(\lambda) d\lambda}$$

$A_{1\alpha}$  and  $A_{2\alpha}$  are not independent but are related by the condition

$$A_{1\alpha} - A_{2\alpha} = \left( \int L_{\alpha}^2(\lambda) B_{\alpha}(\lambda) d\lambda - \int L_{\alpha}(\lambda) C_{\alpha}(\lambda) d\lambda \right) / \int L_{\alpha}^2(\lambda) d\lambda \quad (3.4c)$$

This condition may be obtained by premultiplying (3.4a) by  $L_{\alpha}(\lambda)$  and integrating over  $\lambda$ .

Coulomb and exchange integrals appearing in (3.4a-c) are defined by

$$B_{\alpha}(\lambda) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \left( \int M_{\alpha}^2(\mu) L_{\beta}^2(\lambda') M_{\beta}^2(\mu') \frac{1}{r_{12}} (\lambda'^2 - \mu'^2) \cdot \right. \\ \left. (\lambda'^2 - \mu'^2) d\tau_1 \right) / \int M_{\alpha}^2(\mu) d\mu$$

$$C_{\alpha}(\lambda) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \delta(m_{s_{\alpha}} m_{s_{\beta}}) L_{\beta}(\lambda) \quad .$$

$$\left( \int M_{\alpha}(\mu) M_{\beta}(\mu) L_{\alpha}(\lambda') L_{\beta}(\lambda') M_{\alpha}(\mu') M_{\beta}(\mu') (\lambda^2 - \mu^2) \cdot \right.$$

$$\left. (\lambda'^2 - \mu'^2) \cdot e^{i(m_{\alpha} - m_{\beta})\phi} e^{i(m_{\alpha} - m_{\beta})\phi'} d\tau_1 \right) / \int M_{\alpha}^2(\mu) d\mu$$

where

$$d\tau_1 = d\mu d\mu' d\lambda' d\phi d\phi'$$

$$G_{\alpha}(\mu) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \left( \int L_{\alpha}^2(\lambda) L_{\beta}^2(\lambda') M_{\beta}^2(\mu') (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) \frac{1}{r_{12}} \right. \\ \left. \cdot d\tau_2 \right) / \int L_{\alpha}^2 d\lambda$$

$$H_{\alpha}(\mu) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \delta(m_{s_{\alpha}} m_{s_{\beta}}) M_{\beta}(\mu) \cdot$$

$$\left( \int L_{\alpha}(\lambda) L_{\beta}(\lambda) L_{\alpha}(\lambda') L_{\beta}(\lambda') M_{\alpha}(\mu') M_{\beta}(\mu') (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) \frac{1}{r_{12}} \right. \\ \left. \cdot e^{i(m_{\alpha} - m_{\beta})\phi} e^{i(m_{\alpha} - m_{\beta})\phi'} d\tau_2 \right) / \int L_{\alpha}^2(\lambda) d\lambda$$

where

$$d\tau_2 = d\lambda d\lambda' d\mu' d\phi d\phi'$$

and

$$r_{12} = \frac{R}{2} [\lambda^2 + \lambda'^2 + \mu^2 + \mu'^2 - 2(1 + \lambda\lambda'\mu\mu') \\ - 2((\lambda^2 - 1)(1 - \mu^2)(\lambda'^2 - 1)(1 - \mu'^2))^{\frac{1}{2}} \cos(\phi_1 - \phi_2)]^{\frac{1}{2}}.$$

The set of equations (3.4a), (3.4b) are to be solved for the  $2N$  functions  $L_{\alpha}$  and  $M_{\alpha}$  ( $\alpha=1, \dots, N$ ) and the Lagrange multipliers  $\epsilon_{\alpha\beta}$  subject to the constraints

(i) boundary conditions:

$$L_{\alpha}(\infty) = 0, L_{\alpha}(1) \text{ and } M_{\alpha}(\pm 1) \text{ must be finite for } \alpha=1, \dots, N.$$

(3.4d)

(ii) normalisation and orthogonality:

$$\begin{aligned} \frac{R^3}{8} \int_1^\infty L_\alpha(\lambda) L_\beta(\lambda) M_\alpha(\mu) M_\beta(\mu) (\lambda^2 - \mu^2) d\lambda d\mu &= \delta_{\alpha\beta} \\ \int_{-1}^{+1} M_\alpha(\mu) M_\alpha(\mu) d\mu &= 1 \end{aligned} \quad (3.4e)$$

for  $\alpha=1, \dots, N$ ,  $\beta=\alpha, \dots, N$  and  $\Delta(\alpha, \beta) \neq 0$

To the best of the authors knowledge, this set of equations (3.4a-e) has not previously been solved. The FDNRA provides a very efficient method of solving  $H_2^+$  type differential equations. The additional terms contained in (3.4), as compared with (2.24), do not pose any great difficulties in the use of the algorithm, providing the functions  $B_\alpha(\lambda)$ ,  $C_\alpha(\lambda)$ ,  $D_{\alpha\beta}(\lambda)$ ,  $G_\alpha(\mu)$ ,  $H_\alpha(\mu)$  and  $E_{\alpha\beta}(\mu)$  are considered not to change within a NR iteration. This, in fact, is just a slight modification of the standard SCF method [20].

In most HF-SCF calculations one solves for a particular orbital in the field of the other electrons in orbitals determined by the previous SCF iteration. This procedure is quite satisfactory for atomic calculations, and for molecular calculations when using the methods of Roothaan. However, with (3.4) we have an additional problem. For a given value of  $\alpha$  the coulomb and exchange integrals,  $B_\alpha(\lambda)$  and  $C_\alpha(\lambda)$  contain not only the functions  $L_\beta(\lambda)$  and  $M_\beta(\mu)$  ( $\beta \neq \alpha$ ), but also  $M_\alpha(\mu)$ .

The modification to the SCF procedure is simply that we hold as fixed from the previous SCF iteration all functions within the integrals  $B_\alpha(\lambda)$ ,  $C_\alpha(\lambda)$ ,  $D_{\alpha\beta}(\lambda)$ ,  $G_\alpha(\mu)$ ,  $H_\alpha(\mu)$  and  $E_{\alpha\beta}(\mu)$ . The solution of the set of equations (3.4) is achieved by firstly calculating the functions  $B_\alpha$ ,  $C_\alpha$ ,  $D_{\alpha\beta}$ ,  $G_\alpha$ ,  $H_\alpha$ ,  $E_{\alpha\beta}$  using some suitable starting solution (usually the solution to the single electron problem), solving (2.4) for each orbital in turn using FDNRA, calculating the functions,  $G$  through  $E$ , using the new functions  $L_\alpha$ ,  $M_\alpha$ , ( $\alpha=1, \dots, N$ ) and repeating the calculation. This procedure is repeated until the change in the  $L_\alpha$ 's and  $M_\alpha$ 's is within a required tolerance. At this point the final functions  $L_\alpha$ ,  $M_\alpha$  ( $\alpha=1, \dots, N$ ) are solutions to (2.4) within this tolerance.

Convergence of the SCF iteration just described can be rather slow, especially for heteronuclear molecules. However there are various techniques that may be used to accelerate convergence e.g. see [21].

The most successful technique for this work was to define new functions,

$$\begin{aligned} L_\alpha^{i+1} &= \gamma_\alpha L_\alpha^i + (1-\gamma_\alpha) L_\alpha^{i-1} \\ M_\alpha^{i+1} &= \gamma'_\alpha M_\alpha^{i+1} + (1-\gamma'_\alpha) M_\alpha^{i-1} \end{aligned} \quad \gamma, \gamma' < 1 \quad (3.5)$$

and use these to calculate the coulomb and exchange integrals. The values of  $\gamma, \gamma'$  may be optimized in the following manner.



(i) Calculate  $L_\alpha, M_\alpha$   $\alpha=1, \dots, N$  for three iterations with  $\gamma, \gamma'=1$ .

(ii) Calculate values for  $\gamma, \gamma'$  using

$$\gamma = (L^{i-2} - L^{i-1}) / (L^{i-2} - 2L^{i-1} + L^{i-2})$$

$$\gamma' = (M^{i-2} - M^{i-1}) / (M^{i-2} - 2M^{i-1} + M^{i-2})$$

(iii) Calculate  $L_\alpha, M_\alpha$   $\alpha=1 \dots N$  using (2.5).

(iv) Repeat (i).

Two or three applications of this procedure were sufficient for almost all cases examined.

#### METHOD OF SOLUTION

We now proceed to put equations (3.4) into a form suitable for solution using FDNRA.

As with  $H_2^+$  we make the transformations,

$$X_\alpha(\lambda) = (\lambda^2 - 1)^{1-m/2} L_\alpha(\lambda),$$

$$Y_\alpha(\mu) = (1 - \mu^2)^{1-m/2} M_\alpha(\lambda),$$

(3.6)

$$\zeta = (\lambda - 1) / (c\lambda + c + 1)$$

$$\rho = \frac{\mu}{(a - \mu^2)}$$

In terms of the transformed variables the HF equations become

$$\begin{aligned} & [(1-c\zeta)^2 \zeta (\zeta + 2(1-c\zeta)) \frac{d^2}{d\zeta^2} + (2(m+1) \left( \frac{1+(1-c)\zeta}{1-c\zeta} \right) (1-c\zeta)^2 \\ & + 2c\zeta (\zeta + 2(1-c\zeta)) (1-c\zeta) \frac{d}{d\zeta} - \frac{4m(1-c\zeta)^4}{\zeta(2(1-c)+\zeta)(1+(1-c)\zeta)}] X_\alpha(\zeta) \end{aligned} \quad (3.7a)$$

$$+ m(m+1) + A_{1\alpha} - B_\alpha(\zeta) + P_{\alpha\alpha}^2 \frac{(1+(1-b\zeta))^2}{(1-b\zeta)^2} X_\alpha(\zeta)$$

$$+ C_\alpha(\zeta) + \sum_{\beta \neq \alpha} D_{\alpha\beta}(\zeta) \epsilon_{\alpha\beta} X_\beta(\zeta)$$

$$\left[ \frac{2(2\rho^2(1-a)-1-(1+4a\rho^2)^{\frac{1}{2}})\rho^2(1+4a\rho^2)}{((1+4a\rho^2)^{\frac{1}{2}}-1)^2} \frac{d^2}{d\rho^2} + ((m+1)\rho(1+4a\rho^2)^{\frac{1}{2}} + \right.$$

$$\left. \frac{4\rho((1+4a\rho^2)^{\frac{3}{2}} - (1+6a\rho^2))(2\rho^2(1-a)-1-(1+4a\rho^2)^{\frac{1}{2}})}{((1+4a\rho^2)^{\frac{1}{2}}-1)^3} \right) \frac{d}{d\rho} - A_{2\alpha}$$

$$- \frac{4m(1-(1+4a\rho^2)^{\frac{1}{2}}+4a\rho^2)}{-1+(1+4a\rho^2)^{\frac{1}{2}}+4(1-a)\rho^2} - m(m+1) - R \left( \frac{-1+(1+4a\rho^2)^{\frac{1}{2}}}{2\rho} \right) (Z_a - Z_b)$$

$$- G_\alpha(\rho) - P_{\alpha\alpha}^2 \left( \frac{-1+(1+4a\rho^2)^{\frac{1}{2}}}{2\rho} \right)^2 Y_\alpha(\rho) + \sum_{\beta \neq \alpha} E_{\alpha\beta}(\rho) \epsilon_{\alpha\beta} Y_\beta(\rho)$$

$$+ H_\alpha(\rho) = 0 \quad (3.7b)$$

where the coulomb and exchange integrals are defined as in (3.4) with the dependant and independant variables transformed according to (3.6). Similarly the integrals

$D_{\alpha\beta}$  and  $E_{\alpha\beta}$  are transformed to the new variables.

The separation-constant, normalisation, and orthogonality conditions transform to

$$\int Y_{\alpha}^2 \frac{(-1+(4a\rho^2-1)^{\frac{1}{2}}) d\rho}{(1+4a\rho^2)(2\rho^2(1-a)-1+2(1+4a\rho^2)^{\frac{1}{2}})} - 1 = 0, \quad (3.7c)$$

$$\begin{aligned} & \frac{R^3}{8} \iiint X_{\alpha} X_{\beta} Y_{\alpha} Y_{\beta} \frac{(1-c\zeta)^2}{\zeta^2(2(1-c)+\zeta)} \frac{(-1+(4a\rho^2+1)^{\frac{1}{2}})}{(1+4a\rho^2)(2\rho^2(1-a)-1+2(1+4a\rho^2)^{\frac{1}{2}})} \\ & \cdot \left( \frac{(1+(1-c)\zeta)^2}{(1-c\zeta)} - \frac{(-1+(1+4a\rho^2)^{\frac{1}{2}})^2}{2\rho} \right) e^{i(m_{\alpha}-m_{\beta})\phi} d\rho d\zeta d\phi = \delta_{\alpha\beta} \end{aligned} \quad (3.7d)$$

Boundary conditions are

$$X(0) = X\left(\frac{1}{c}\right) = 0, \quad (3.7e)$$

$$Y\left(\frac{-1}{a-1}\right) = Y\left(\frac{1}{a-1}\right) = 0.$$

Equations (3.7) are now translated into finite difference form using the notation and approximations of equations (2.18) through (2.20). For the present case these equations become,

$$\begin{aligned} & B(\zeta_i)(X_{i+1}^{\alpha} - 2X_i^{\alpha} + X_{i-1}^{\alpha})/h_1^2 + C(\zeta_i)(X_{i+1}^{\alpha} - X_{i-1}^{\alpha})/2/h_1 \\ & + (D(\zeta_i) - B_{\alpha}(\zeta_i) + A_{1\alpha} - \frac{p_{\alpha}^2(1+(1-c\zeta_i))^2}{(1-c\zeta_i)}) X_i^{\alpha} + C_{\alpha}(\zeta_i) \end{aligned} \quad (3.8a)$$

$$+ \sum_{\beta \neq \alpha} D_{\alpha\beta}(\zeta_i) \varepsilon_{\alpha\beta} X_i^{\beta} = 0$$

$$\begin{aligned}
& B'(\rho_k) (Y_{k+1}^\alpha - 2Y_k^\alpha + Y_{k-1}^\alpha) / h_2^2 + C'(\rho_k) (Y_{k+1}^\alpha - Y_{k-1}^\alpha) / 2h_2 \\
& + (D'(\rho_k) - G_\alpha(\rho_k) - A_{2\alpha} + \frac{P^2(\sqrt{1+4a\rho_k^2} - 1)}{8\rho_k^2}) Y_{k+1}^\alpha + H_\alpha(\rho_k) + \sum_{\beta \neq \alpha} E_{\alpha\beta}(\rho_k) \epsilon_{\alpha\beta} Y_k^\beta = 0
\end{aligned}
\tag{3.8b}$$

The finite difference form of the coulomb and exchange integrals and the method of evaluating them is left to appendix B. Suffice it to say at this point that the rather daunting prospect of five dimensional numerical integration can be reduced to the equivalent of the sum of the products of five one dimensional integrals.

Considering one spin-orbital at a time, (3.8a) and (3.8b) are very similar to (2.22) and (2.23). When normalisation conditions (3.7c), (3.7d) are included in finite difference form a variation on the method used to solve (2.22) through (2.24) may be used to solve (3.8a), (3.8b). There is of course the additional complication of coulomb and exchange integrals and the off diagonal Lagrange multipliers. The method for dealing with the coulomb and exchange integrals has already been described. We have one orthogonality condition for each  $\epsilon_{\alpha\beta}$ ,  $\beta \neq \alpha$  and with a particular ordering of unknowns may retain the almost tridiagonal form of the Jacobian matrix. Using the notation and ordering of the unknowns described in chapter II, we have,

$$P_\alpha^k = Y_\alpha^k, \quad k = 1, 2 \dots N_1 - 1,$$

$$P_{\alpha}^{k+N_1-1} = X_{\alpha}^k, \quad K = 1, 2 \dots N_2-1,$$

$$P_{\alpha}^{N_1+N_2-1} = P_{\alpha\alpha}^2, \quad (3.9)$$

$$P_{\alpha}^{N_1+N_2} = A_{1\alpha},$$

$$P_{\alpha}^{N_1+N_2+k} = P_{\alpha\beta}^2, \quad k = 1, 2 \dots M.$$

M is the number of molecular spin orbitals to which  $\phi_{\alpha}$  is constrained to be orthogonal.

We now have  $N_1+N_2+M$  equations in the unknowns  $P_k$ ,  $k = 1, 2 \dots N_1+N_2+M$  and they may be solved using a GNRI.

## RESULTS

Calculations were performed for a range of nuclear separations for the  $^1\Sigma_g^+$  state of  $H_2$ . These are presented graphically in Fig (3.1). More detailed results for this state and the  $^3\Sigma_u^+$  state are presented in Tables (3.1), (3.2). Here a Richardson extrapolation [17] has been used to determine the results in the  $h \rightarrow 0$  limit. A comparison with calculations based upon other methods is given in Table (3.3). It should be noted that the calculation described here represents an improvement over other methods assuming the same simple form for the spin-orbitals [19],[14].

It is thought however that the assumed factorization of the spin-orbitals into the form,

$$\phi = L(\lambda)M(\mu)e^{im\phi}/\sqrt{2\pi} \quad ,$$

is the reason for the discrepancy between our results and those of Roothan [23]. For  $H_2$  the difference is small. For larger diatomic molecules the results are not so encouraging. Results for  $Li_2$  ( $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$ ) differ markedly from the accepted HF result. Again this is believed to be due to the factored form assumed for the spin orbitals.

There are two obvious ways of overcoming this situation. The first is to express each S.O. in the form

$$\phi_\alpha = \left( \sum_{k=1}^M a_k L_\alpha^k(\lambda) M_\alpha^k(\mu) \right) e^{im_\alpha}/\sqrt{2\pi} \quad .$$

Varying each  $L_\alpha^k$  and  $M_\alpha^k$  gives a set of integrodifferential equations for the  $L_\alpha^k$ 's and  $M_\alpha^k$ 's. This method is quite feasible using an extension of the methods described in this chapter. However this would require considerable computational effort to solve for the  $\phi_\alpha^k$ 's and the coefficient, with the same effort one can perform a full multiconfiguration calculation. We have opted for the latter approach.

Table 3.1: Neville Table for the Total Energy of the  $(1s\sigma_g)^2 1\Sigma_g^+$  state of  $H_2$  at  $R = 1.4$  a.u.

$N_1=N_2$ =number  
of mesh points

80	-1.133357	-1.133406	-1.133456	-1.133462	-1.133461
100	-1.133375	-1.133434	-1.133460	-1.133462	
120	-1.133393	-1.133447	-1.133461		
140	-1.133407	-1.133453			
160	-1.133418				

Table 3.2:  $(1s\sigma_g)(2p\sigma_u) 3\Sigma_u^+$  state of  $H_2$   $R = 1.4$  a.u.

$N_1=N_2$ =number  
of mesh points

80	-.774093	-.776908	-.777355	-.777542	-.777646
100	-.775098	-.777155	-.777480	-.777620	
120	-.775721	-.777313	-.777565		
140	-.776141	-.777423			
160	-.776440				

Table 3.3\*

Description of calculation	Nonlinear Variational Parameters	-E	Ref.
1s,2s,2p $\sigma$ STO's on each center	1	1.13211	[34]
ETO's Approximate potential		1.13297	[19]
12 Floating 1s Gaussians	12	1.13342	[35]
5 <sup>S</sup> + 2 <sup>P</sup> GTO's	2	1.13346	[36]
Finite Difference factored Orbitals		1.13346	
1s,2s,2p $\sigma$ STO's on each center	3	1.13349	[37]
H <sub>2</sub> <sup>+</sup> type ETO's	2	1.13350	[38]
2 integral ETO's	4	1.13357	[39]
H <sub>2</sub> <sup>+</sup> type ETO's	2	1.13360	[38]
2 non-integral ETO's	6	1.13361	[39]
3-D HF limit		1.13363	[23]

Table 3.4: Neville Table for Ground State of Li<sub>2</sub> at R = 5 a.u.

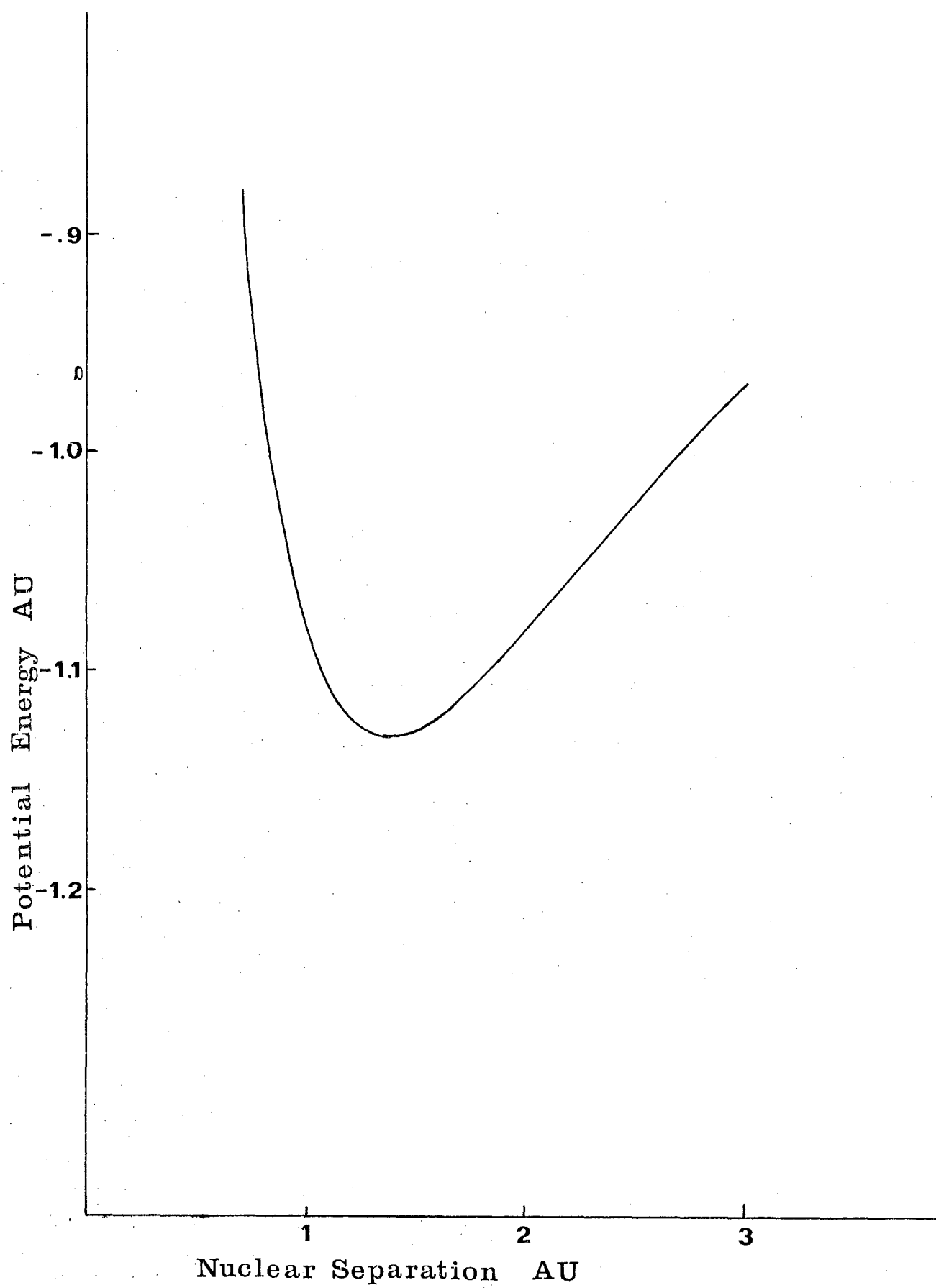
N<sub>1</sub>=N<sub>2</sub>=No of  
Mesh Points

80	-15.19515	-15.19525	-15.17075
98	-15.18862	-15.18269	
116	-15.18274		

\*

This table in the main is taken Llaguno et. al. [38].



Potential Energy of  $H_2$  Fig 31

MULTICONFIGURATION HARTREE-FOCK EQUATIONS  
FOR DIATOMIC MOLECULES

In order to overcome the inaccuracies in expectation values calculated using single configuration factored HF orbitals we consider the wavefunction of a molecule to be a sum of Slater determinants. (SD's). While this is certainly not a new idea (see [24], [25]), previously all molecular and some atomic calculations have used the expansion methods of Roothan [26].

Here we solve for the SO's composing the Slater determinants in finite-difference form.

We write the total wavefunction

$$\psi = \sum_{I=1}^M a_I \psi_I \quad (4.1)$$

where

$$\psi_I = \phi_1^I(1) \phi_2^I(2), \dots \phi_N^I(N),$$

and

$$\phi_{\alpha}^I = \frac{1}{\sqrt{2\pi}} L_{\alpha}^I(\lambda) M_{\alpha}^I(\mu) e^{im_{s\alpha}^I \phi} \chi_{\frac{1}{2}}^{m_{s\alpha}^I},$$

$\lambda, \mu$  and  $\phi$  are the usual confocal elliptic coordinates and  $\chi_{\frac{1}{2}}^{m_{s\alpha}^I}$  represents the spinors  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$  and  $\begin{pmatrix} 0 \\ 1 \end{pmatrix}$  for  $m_{s\alpha} = \pm \frac{1}{2}$  respectively

The  $\psi_I$  ( $I > 1$ ) are selected from the set of all excited configurations belonging to the same symmetry species as the state under consideration. This set of  $\psi_I$ 's forms a N electron basis with which to expand the total wavefunction  $\psi$ .

Hamiltonian be stationary with respect to small variations in the expansion coefficients  $a_I$  and the molecular SO's simultaneously, much shorter expansions than with configuration interaction should result.

Generally, we can have both excited and unexcited SO's in the SD's,  $\psi_I$  ( $I > 1$ ). The latter, if any, are identical to corresponding SO's in  $\psi_1$  and are labelled with the same value of  $\alpha$ . In order to simplify the variational equations as much as possible, we require that

$$\langle \phi_\alpha^I | \phi_\beta^J \rangle = \delta_{\alpha\beta} \quad (4.2)$$

for all values of  $I$  and  $J$ , except when one or both of the SO's,  $\phi_\alpha^I$  and  $\phi_\alpha^J$ , are excited, in which case

$$\langle \phi_\alpha^I | \phi_\alpha^J \rangle = 0 \quad (4.3)$$

In other words, all of the SO's in all the SD's form an orthonormal set.

With these restrictions on the wavefunction the expectation value of the Hamiltonian is

$$\langle H \rangle = \sum_{IJ} a_I a_J \left( \sum_{\alpha} \langle \phi_\alpha^I(1) | F_1 | \phi_\alpha^J(1) \rangle \right) \quad (4.4)$$

$$+ \frac{1}{2} \sum_{\alpha \neq \beta} \langle \phi_{\alpha}^I(1) \phi_{\beta}^I(2) | F_{12} | \phi_{\alpha}^J(1) \phi_{\beta}^J(2) \phi_{\beta}(2) - \phi_{\beta}^J(1) \phi_{\alpha}^J(2) \rangle , \quad (4.4)$$

where

$$F_1 = -\frac{1}{2} \nabla_1^2 - \frac{Z_a}{r_{a1}} - \frac{Z_b}{r_{b1}} ,$$

and

$$F_{12} = \frac{1}{r_{12}} .$$

Varying the expansion coefficients subject to the constraint of total normalisation results in the matrix eigenvalue problem.

$$\sum_J \langle \psi_I | H | \psi_J \rangle a_J - \lambda a_I = 0 \quad (4.5)$$

Obtaining variational equations for the orbitals is more difficult. We form the functional

$$\begin{aligned} \theta = & \sum_{IJ} a_I a_J \left( \sum_{\alpha} \langle \phi_{\alpha}^I(1) | F_1 | \phi_{\alpha}^J(1) \rangle \right. \\ & + \frac{1}{2} \sum_{\alpha \beta} \langle \phi_{\alpha}^I(1) \phi_{\beta}^I(2) | F_{12} | \phi_{\alpha}^J(1) \phi_{\beta}^J(2) - \phi_{\beta}^J(1) \phi_{\alpha}^J(2) \rangle \\ & + \sum_{\alpha \beta} \lambda_{\alpha \beta}^{IJ} \langle \phi_{\alpha}^I | \phi_{\beta}^J \rangle \quad , \end{aligned} \quad (4.6)$$

where the  $\lambda_{\alpha \beta}^{IJ}$  are Lagrange multipliers associated with the constraints (4.2). Demanding that  $\delta\theta=0$  w.r.t. small variations in  $L_{\alpha}^K$  and

$M_\alpha^K$  results in a set of coupled equations for the  $L_\alpha^K$  and  $M_\alpha^K$ . We have, varying  $L_\alpha^K$  and rearranging,

$$\begin{aligned}
 & a_K \sum_J a_J (I_\alpha^{KJ} [\frac{\partial}{\partial \lambda} (\lambda^2 - 1) \frac{\partial}{\partial \lambda} - \frac{m_\alpha^{J^2}}{\lambda^2 - 1} + R(Z_a + Z_b)\lambda \\
 & + A_{1\alpha}^{KJ} - B_\alpha^{KJ}(\lambda) + \epsilon_{\alpha\alpha}^{KJ} \lambda^2] L_\alpha^J(\lambda) \\
 & + C_\alpha^{KJ}(\lambda) + \sum_{\beta \neq \alpha} D_{\alpha\beta}^{KJ}(\lambda) \epsilon_{\alpha\beta}^{KJ} L_\beta^J(\lambda)) = 0, \quad (4.7)
 \end{aligned}$$

where

$$I_\alpha^{KJ} = \int_{-1}^{+1} M_\alpha^K(\mu) M_\alpha^J(\mu) d\mu \cdot \delta_{m_\alpha^K m_\alpha^J} \cdot \Delta(J, K) \quad (4.8)$$

$$\Delta(K, J) = \prod_{\substack{\gamma=1 \\ \neq \alpha}}^N \langle \phi_\gamma^K | \phi_\gamma^J \rangle$$

$$\begin{aligned}
 B_\alpha^{KJ}(\lambda) &= \frac{R^5}{64\pi^2} \cdot \sum_{\beta \neq \alpha} \int \frac{L_\beta^K(\lambda') L_\beta^J(\lambda') M_\beta^J(\mu') M_\beta^K(\mu') M_\alpha^K(\mu) M_\beta^J(\mu)}{r_{12}} \\
 &\cdot (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) d\lambda' d\mu d\mu' d\phi d\phi' \quad (4.9)
 \end{aligned}$$

$$C_\alpha^{KJ}(\lambda) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \delta(m_{s_\alpha}^K m_{s_\beta}^J).$$

$$\begin{aligned}
 & \int \frac{L_\beta^J(\lambda') L_\alpha^J(\lambda') M_\beta^J(\mu') M_\alpha^J(\mu') M_\alpha^J(\mu) M_\alpha^K(\mu)}{r_{12}} \\
 & \cdot (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) \cdot e^{i(m_\beta^J - m_\alpha^J)\phi'} \cdot e^{i(m_\alpha^K - m_\beta^K)\phi} \\
 & \cdot d\lambda' d\mu d\mu' d\phi d\phi' \quad (4.10)
 \end{aligned}$$

$$A_{1\alpha}^{KJ} = \int_{-1}^{+1} M_{\alpha}^K \left( \frac{\partial}{\partial \mu} (1-\mu^2) \frac{\partial}{\partial \mu} - \frac{m_{\alpha}^{J^2}}{(1-\mu^2)} - (Z_a - Z_b) R \mu \right. \\ \left. - \epsilon_{\alpha\alpha}^{KJ} \mu^2 \right) M_{\alpha}^J d\mu \quad (4.11)$$

$$D_{\alpha\beta}^{KJ}(\lambda) = (\lambda^2 \int M_{\alpha}^K(\mu) M_{\beta}^J(\mu) d\mu - \int \mu^2 M_{\alpha}^K(\mu) M_{\beta}^J(\mu) d\mu) \quad (4.12)$$

Similarly, varying  $M_{\alpha}^K$  and rearranging,

$$a_K \left( \sum_J I_{\alpha}^{KJ} a_J \left[ \frac{\partial}{\partial \mu} (1-\mu^2) \frac{\partial}{\partial \mu} - \frac{m_{\alpha}^{J^2}}{(1-\mu^2)} - R(Z_a - Z_b) \mu \right. \right. \right. \\ \left. \left. - A_{2\alpha}^{KJ} - G_{\alpha}^{KJ}(\mu) - \epsilon_{\alpha\alpha}^{KJ} \mu^2 \right] M_{\alpha}^J(\mu) + H_{\alpha}^{KJ}(\mu) \right. \\ \left. + \sum_{\beta \neq \alpha} \epsilon_{\alpha\beta}^{KJ} E_{\alpha\beta}^{KJ}(\mu) M_{\beta}^J(\mu) \right) = 0 \quad (4.12)$$

where

$$G_{\alpha}^{KJ}(\mu) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \int \frac{L_{\alpha}^K(\lambda') L_{\alpha}^J(\lambda) L_{\beta}^J(\lambda) L_{\beta}^K(\lambda') M_{\beta}^J(\mu')}{r_{12}} \\ \cdot M_{\beta}^K(\mu') (\lambda^2 - \mu^2) \cdot (\lambda'^2 - \mu'^2) d\lambda d\lambda' d\mu' d\phi d\phi' \quad (4.13)$$

$$H_{\alpha}^{KJ}(\mu) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \delta(m_{s_{\alpha}}^K m_{s_{\beta}}^J) \int \frac{L_{\alpha}^K(\lambda) L_{\beta}^K(\lambda) L_{\alpha}^J(\lambda') L_{\beta}^J(\lambda') M_{\alpha}^J(\mu') M_{\beta}^J(\mu')}{r_{12}} \\ \cdot (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) e^{i(m_{\beta}^J - m_{\alpha}^J)\phi'} e^{i(m_{\alpha}^K - m_{\beta}^K)\phi} \\ d\lambda d\lambda' d\mu' d\phi d\phi' \quad (4.14)$$

$$A_{2\alpha}^{KJ} = \int L_{\alpha}^K(\lambda) \left[ \frac{\partial}{\partial \lambda} (\lambda^2 - 1) \frac{\partial}{\partial \lambda} - \frac{m_{\alpha}^{J^2}}{\lambda^2 - 1} + R(Z_a + Z_b) \lambda + \epsilon_{\alpha\alpha}^{KJ} \lambda^2 \right] L_{\alpha}^J(\lambda) d\lambda \quad (4.15)$$

$$E_{\alpha\beta}^{KJ}(\mu) = \int L_{\alpha}^K(\lambda) L_{\beta}^J(\lambda) \lambda^2 d\lambda - \mu^2 \int L_{\alpha}^K(\lambda) L_{\beta}^J(\lambda) \quad (4.16)$$

These equations (4.7) - (4.16) comprise a set of 2MN coupled integrodifferential equations for the  $L_{\alpha}^K$  and  $M_{\alpha}^K$ .

It should be noted that for any particular calculation many of the differential coupling terms will be zero resulting in considerable simplification of (4.7) and (4.12). This results from the fact that the product,

$$\sum_{\substack{\gamma=1 \\ \gamma \neq \alpha}}^N \langle \phi_{\gamma}^K | \phi_{\gamma}^J \rangle = 0 \quad ,$$

when  $\psi^K$  and  $\psi^J$  differ by more than one S.O.

An additional set of equations relating the  $A_{1\alpha}^{KJ}$ 's and  $A_{2\alpha}^{KJ}$ 's may be derived by premultiplying (4.7) by  $L_{\alpha}^K(\lambda)$  and integrating over  $\lambda$  from 1 to  $\infty$ .

$$\begin{aligned} \sum_{J=1}^N a_J I_{\alpha}^{KJ} (A_{1\alpha}^{KJ} - A_{2\alpha}^{KJ}) &= \sum_J a_J \left( \int_1^{\infty} B_{\alpha}^{KJ} L_{\alpha}^K(\lambda) L_{\alpha}^J(\lambda) d\lambda \right. \\ &\quad \left. - \int_1^{\infty} C_{\alpha}^{KJ}(\lambda) L_{\alpha}^K(\lambda) d\lambda \right) \end{aligned} \quad (4.17)$$

Equations (4.7) through (4.17) are to be solved using a generalisation of the FDNRA described in Chapter II. Transforming (4.7) through (4.17) according to (2.7) and writing them in terms of new independent variables  $\zeta$  and  $\rho$  defined in (2.12), (2.13) puts the equations in a form suitable for the application of the FDNRA. In terms of the new variables equations (4.7) and (4.12) become,

$$\begin{aligned}
& a_K \sum_J (I_{\alpha}^{KJ} (B(\zeta)) \frac{d^2}{d\zeta^2} + C(\zeta) \frac{d}{d\zeta} + D(\zeta) \\
& + A_{1\alpha}^{KJ} + (P^2)_{\alpha\alpha}^{KJ} \frac{(1+(1-c\zeta))^2}{(1-c\zeta)^2} - B_{\alpha}^{KJ}(\zeta) X_{\alpha}^J(\zeta) \\
& + \frac{2\zeta+(1-2c)\zeta^2}{(1-c\zeta)^2} C_{\alpha}^{KJ}(\zeta) + \sum_{\beta \neq \alpha} D_{\alpha\beta}^{KJ} \epsilon_{\alpha\beta}^{KJ} X_{\beta}^J(\zeta)) = 0 \quad (4.18)
\end{aligned}$$

$$\begin{aligned}
& a_K \sum_J (I_{\alpha}^{KJ} (B'(\rho)) \frac{d^2}{d\rho^2} + C'(\rho) \frac{d}{d\rho} + D'(\rho) - A_{2\alpha}^{KJ} \\
& - (P^2)_{\alpha\alpha}^{KJ} \frac{((+4a\rho^2)^{\frac{1}{2}}-1)}{8\rho^2} - G_{\alpha}^{KJ}(\rho) Y_{\alpha}^J(\rho) + \frac{(4\rho^2-(\sqrt{1+4a\rho^2}-1)}{4\rho^2} H_{\alpha}^{KJ}(\rho) \\
& + \sum_{\beta \neq \alpha} E_{\alpha\beta}^{KJ}(\rho) Y_{\beta}^J(\rho)) = 0 \quad (4.19)
\end{aligned}$$

$$K = 1, \dots, M \quad \text{and} \quad \alpha = 1, \dots, N,$$

where

$B(\zeta)$ ,  $C(\zeta)$ ,  $D(\zeta)$ ,  $B'(\zeta)$ ,  $C'(\zeta)$  and  $D'(\zeta)$  are defined as in equation (2.14b) and (2.15b). Equations (4.18) and (4.19) are to be solved subject to boundary value conditions (2.4) on each  $L_{\alpha}^I$  and  $M_{\alpha}^I$   $I=1, \dots, M$ ,  $\alpha=1, \dots, N$ , normalisation and orthogonality constraints (4.3). We also demand that

$$\int M_{\alpha}^I M_{\alpha}^I d\mu = 1 \quad (4.20)$$

to ensure numerical stability in the solution. Using the procedure described in Chapter II equations (4.18), (4.19), (r.17) and their associated constraints may be approximated by a set of simultaneous algebraic equations.



The solution of these equations using the FDNRA is described in the next section.

#### METHOD OF SOLUTION

The method used is similar to that used in the solution of the HF equations described in Chapter III. There are, however, several differences in the application of the FDNRA to the MCHF problem. We shall therefore describe its application to this problem in some detail.

The general strategy for the solution of (4.18) and (4.19) is

(i) Estimate a set of expansion coefficients  $a_K$ ,  $K = 1, \dots M$ .

These may be obtained by solving the matrix eigenvalue problem (4.2) using HF wavefunctions to calculate the matrix elements.

(ii) Solve (4.18) and (4.19) for the  $L_\alpha^K$  and  $M_\alpha^K$ . The integrals (4.8) - (4.10), (4.12), (4.13), (4.16) are dealt with as in the HF equations using a SCF iteration technique. The difference between the solution of the HF and MCHF equations is that in the latter case all spin orbitals of all configurations may be solved for simultaneously within a SCF iteration.

This simplifies the treatment of the differential coupling terms and also improves the stability of the SCF iteration [26].

(iii) The  $L_{\alpha}^K$  and  $M_{\alpha}^K$  calculated in (ii) are used to recalculate matrix elements for (4.2), and (4.2) is then solved for a new set of expansion coefficients  $a_K$ ,  $K = 1, \dots, M$ .

(iv) Procedures (ii) and (iii) are repeated until the difference between two consecutive sets of expansion coefficients is within a chosen tolerance.

#### FDNRA APPLIED TO SIMULTANEOUS DIFFERENTIAL EQUATIONS

Generalising the notation of Chapter II we have, after dividing the  $\zeta$  axis into  $N_1$  mesh points and the  $\rho$  axis into  $N_2$  mesh points,

$$\begin{aligned}\zeta_k &= kh_1, \\ \rho_k &= kh_2,\end{aligned}\tag{4.21}$$

where

$$\begin{aligned}h_1 &= 1/c/(N_1+1), \\ h_2 &= 2/(A-1)/(N_2+1),\end{aligned}$$

and

$$\begin{aligned}X_{\alpha K}^J &= X_{\alpha}^J(\zeta_K) \\ Y_{\alpha K}^J &= Y_{\alpha}^J(\rho_K)\end{aligned}\tag{4.22}$$

Unknowns which must be solved for are

$$X_{\alpha k}^J, \quad J = 1, \dots, M; \quad \alpha = 1, \dots, N; \quad k = 1, \dots, N_1$$

$$Y_{\alpha K}^J, \quad J = 1, \dots, M, \quad \alpha = 1, \dots, N, \quad k = 1, \dots, N_2,$$

$$A_{1\alpha}^{JJ}, A_{2\alpha}^{JJ}, \quad J = 1, \dots, M; \quad \alpha = 1, \dots, N,$$

and

$$\epsilon_{\alpha\alpha}^{JJ}, \quad J = 1, \dots, M; \quad \alpha = 1, \dots, N.$$

Unknowns which may have to be solved for are

$$\epsilon_{\alpha\beta}^{KJ}, \quad K \geq J = 1, \dots, M, \quad \alpha, \beta = 1, \dots, N,$$

and

$$A_{1\alpha}^{KJ}, A_{2\alpha}^{KJ}, \quad K > J = 1, \dots, M, \quad \alpha = 1, \dots, N.$$

which of these unknowns must be solved for can only be determined when considering specific cases.

When orthogonality between two spin orbitals is automatic, then the Lagrange multiplier associated with this constraint may be taken as zero and dropped from the list of unknowns. When  $I_{\alpha}^{KJ}$  and  $I'_{\alpha}^{KJ}$  are zero,  $A_{1\alpha}^{KJ}$  and  $A_{2\alpha}^{KJ}$  may be dropped from the unknowns.

$A_{1\alpha}^{KJ}$  and  $A_{2\alpha}^{KJ}$   $k \neq J$  are calculated explicitly each SCF iteration so these may be eliminated from the unknowns within a NR iteration.  $A_{2\alpha}^{JJ}$  is not independent of  $A_{1\alpha}^{JJ}$  but connected by (4.17) and so may also be dropped.

The remaining unknowns are solved for using a GNRI.

By using a particular ordering of the unknowns an almost block tridiagonal Jacobian matrix is obtained and quick inversion methods may be used with this [32].

The solution vector  $\underline{p}$  is defined as

$$\begin{aligned}
 P_{J+(\alpha-1)M+(k-1)MN} &= X_{\alpha k}^J \\
 P_{N_1NM+J+(\alpha-1)M+(\ell-1)NM} &= Y_{\alpha k}^J
 \end{aligned}
 \left. \begin{aligned}
 &J=1, \dots M, \\
 &\alpha=1, \dots N, \\
 &k=1, \dots N_1 \\
 &\ell=1, \dots N_2
 \end{aligned} \right\}$$

(4.23)

$$\begin{aligned}
 P_{N_1NM+N_2NM+\alpha+(J-1)M} &= (P^2)_{\alpha\alpha}^{JJ} \\
 P_{N_1NM+N_2NM+\alpha+(J-1)M+M} &= A_{\alpha\alpha}^{JJ}
 \end{aligned}
 \left. \begin{aligned}
 &J=1, \dots M, \\
 &\alpha=1, \dots N
 \end{aligned} \right\}$$

$$P_{N_1NM+N_2NM+2M+N+L} = \epsilon_{\alpha\beta}^{kJ}, \quad L = 1, \dots S$$

where  $S$  is the number of off-diagonal Lagrange multipliers. Ordering of the off-diagonal multipliers is not important providing it is consistent throughout the calculation. The purpose of this ordering of unknowns is to arrange the values of  $X_{\alpha}^J$  for each mesh point consecutively in the  $\underline{P}$  vector. Thus the first  $M$  positions in the vector contain  $X_{\alpha 1}^J$ ,  $J=1, \dots M$ .

Similarly the next  $M$  positions are occupied by the values of  $X_{\alpha}^J$  at the second mesh point and so on.

Since the differential coupling in a finite difference approximation depends only on the values  $X_{\alpha}^J$  or  $Y_{\alpha}^J$  at a particular mesh point, or at one point either side of it, the Jacobian matrix again takes on a form suitable for quick inversion using the methods described in appendix 1.

The Jacobian matrix takes on the almost block tridiagonal form shown in fig. 4.1.

#### THE GROUND STATE OF HYDROGEN

As a test of the method calculations of total energy of the hydrogen molecule were carried out for a range of nuclear separations.

Four configurations were chosen to make up the total wavefunction. These were:

$$\psi_1(1\sigma_g^2), \psi_2(1\sigma_u^2), \psi_3(2\sigma_g^2), \psi_4(1\pi_u^2).$$

In order to satisfy the antisymmetry principle  $\psi_4$  must be the sum of two determinants i.e.

$$\psi_4 = \frac{1}{\sqrt{2}} (\phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)) (\chi_1^1(1)\chi_1^{-1}(2) - \chi_1^1(2)\chi_1^{-1}(1)), \quad (4.24)$$

where  $\phi_1$  and  $\phi_2$  have angular momentum projections of +1 and -1 respectively but have the same  $\lambda$  and  $\mu$  functions. X

Since all these configurations differ by more than one spin orbital equations (4.18) and (4.19) will not have any differential coupling terms.

This results in a considerable simplification and (4.18) and (4.19) become

$$(B(\zeta)\frac{d^2}{d\zeta^2} + C(\zeta)\frac{d}{d\zeta} + D(\zeta) + A_1^{KK} + \epsilon_{\alpha\alpha}^{KK}\lambda^2 - B_{\alpha}^{KK}(\zeta))X_{\alpha}^K(\zeta)$$

$$+ \sum_{J \neq K} \frac{a_J}{a_K} (-B_{\alpha}^{KJ}(\zeta) X_{\alpha}^J(\zeta) + D_{\alpha\alpha}^{KJ} \epsilon_{\alpha\alpha}^{KJ} X_{\alpha}^J) = 0, \quad (4.25)$$

$$\begin{aligned} & (I_{\alpha\alpha}^{KK} (B'(\rho) \frac{d^2}{d\rho^2} + C'(\rho) \frac{d}{d\rho} + D'(\rho) - A_{2\alpha}^{KK} - \epsilon_{\alpha\alpha}^{KK} \mu^2) - G_{\alpha}^{KK}) Y_{\alpha}^J \\ & + \sum_{J \neq K} \frac{a_J}{a_K} (-G_{\alpha}^{KJ}(\rho) Y_{\alpha}^J(\rho) + E_{\alpha\alpha}^{KJ}(\rho) \epsilon_{\alpha\alpha}^{KJ} Y_{\alpha}^J(\rho)) = 0. \end{aligned} \quad (4.26)$$

From symmetry we have

$$\begin{aligned} \epsilon_{11}^1 &= 0, \\ \epsilon_{11}^4 &= 0. \end{aligned}$$

Equations (4.25) and (4.26) are identical to the HF equations (3.4 a-e) with the exchange term replaced by

$$\sum_{J \neq K} \frac{a_J}{a_K} (-B_{\alpha}^{KJ}(\zeta) X_{\alpha}^J(\zeta))$$

in the  $\zeta$  equation and

$$\sum_{J \neq K} \frac{a_J}{a_K} (-G_{\alpha}^{KJ}(\rho) Y_{\alpha}^J(\rho))$$

in the  $\rho$  equation.

A closer examination of these additional terms makes apparent a simplification which allows us to compute a close approximation to them with little loss in accuracy.

If we consider the relative sizes of the expansion coefficients  $a_K$   $K = 1, M$ , one of them (and possibly two

for large nuclear separation) will be much larger than the others. Assuming the largest coefficient is  $a_1$ , say, then  $\frac{a_J}{a_1}$  ( $J \neq 1$ ) will be small and may be neglected. Also  $\frac{a_1}{a_J} \gg \frac{a_K}{a_J}$   $J \neq K, J \neq 1$ . For a typical case  $\frac{a_1}{a_J} \approx 10 \times \frac{a_K}{a_J}$ , and so we may also neglect terms in the exchange term other than the dominant one. Using this approximation results in a large saving in computer time.

Although this was not an important consideration for  $H_2$  and it was not used, for larger molecules it is well worth considering.

Since there are no differential coupling terms in (4.25 - 4.26) they were solved (for a given set of expansion coefficients) in exactly the same manner as the HF equations. This is described in Chapter III.

## RESULTS

Calculations were performed for a range of nuclear separations between 1 and 5 a.u. The effect of  $\pi$  states in the basis set was investigated at equilibrium separation (1.4 a.u.). In Fig 4.1 the total energy of the molecule as a function of internuclear separation is given. The flexibility of the MCHF wavefunction has completely overcome the deficiency of factorized orbitals found in the simple HF case. We see from Fig. 4.1 that very good agreement with the results of Kolas and Roothaan [23] is obtained. Closer agreement could be obtained by increasing the length of the MCHF expansion.

In Fig 4.2 the variation of expansion coefficients for the  $1\sigma_g^2$ ,  $2\sigma_g^2$  and  $1\sigma_u^2$  states are presented. The dominant states for large internuclear separation are  $1\sigma_g^2$  and  $1\sigma_u^2$ . It is the inclusion of the  $1\sigma_u^2$  state that causes the total energy of the molecule to approach the correct asymptotic limit for large internuclear separation.

Detailed results for equilibrium separation are given in Table 4.1. Here a Richardson extrapolation [17] has been performed on results from a range of mesh spacings to estimate the  $h \rightarrow 0$  limit.

Table 4.1: Neville Table for potential energy of  $H_2$  at  
 $R = 1.4$  configuration MCHF expansion

N

80	-1.1682756			
		-1.1650314		
98	-1.1672107		-1.1649773	
		-1.1650272		-1.1648733
116	-1.1665966		-1.1649113	
		-1.1649737		
134	-1.1661929			

Coefficient of  $2\sigma_g^2$

80	-.057221728			
		-.057116092		
98	-0.57186807		-.057093224	
		-.057104183		-.056980611
116	-.057163341		-.057021152	
		-.057665805		
134	-.057139064			

Coefficient of  $2\sigma_g^2$

80	.99141378			
		.99150485		
98	.99144389		.99150726	
		.99150607		.99124493
116	.99146155		.99133934	
		.99142901		
134	.99145345			



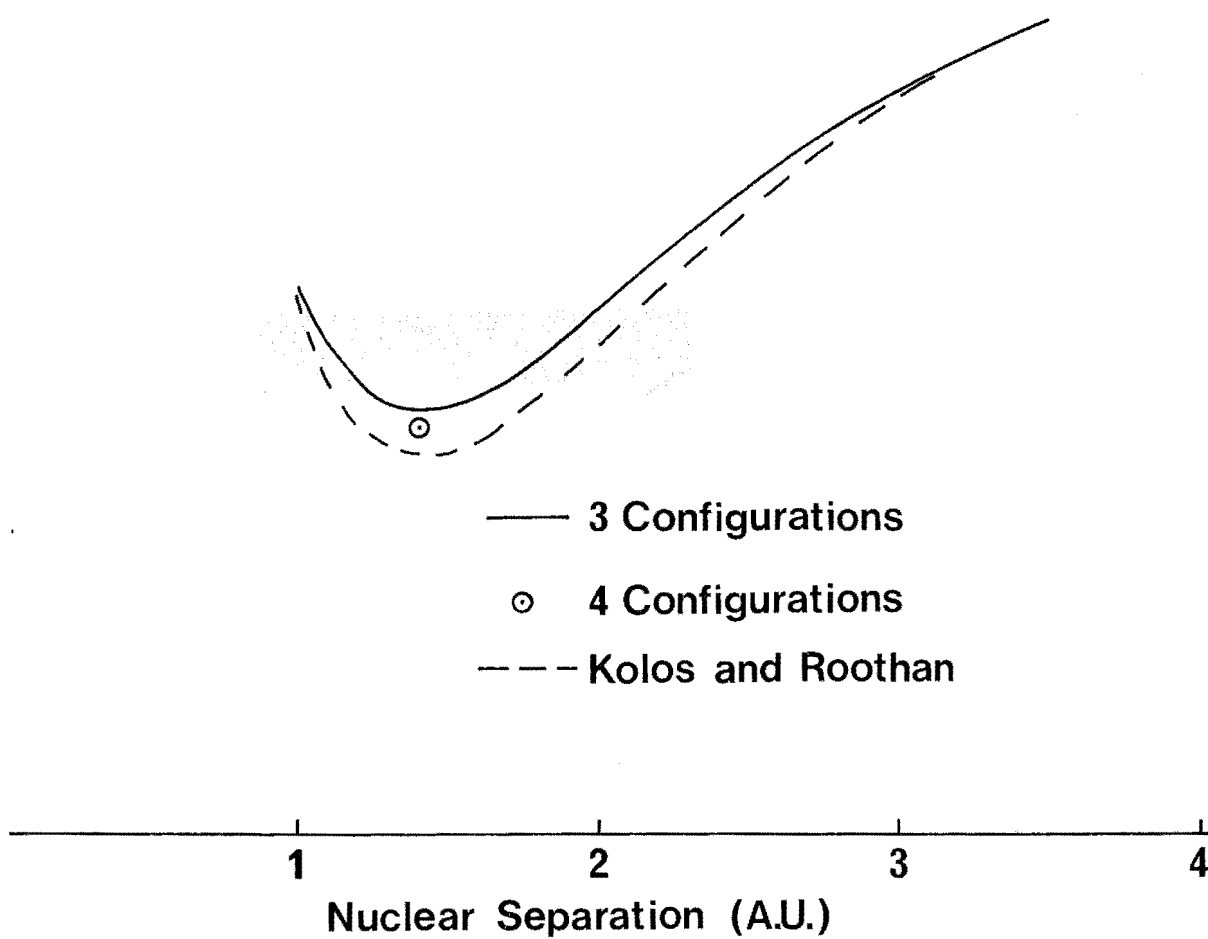
Coefficient of  $(1\pi_u)^2$ 

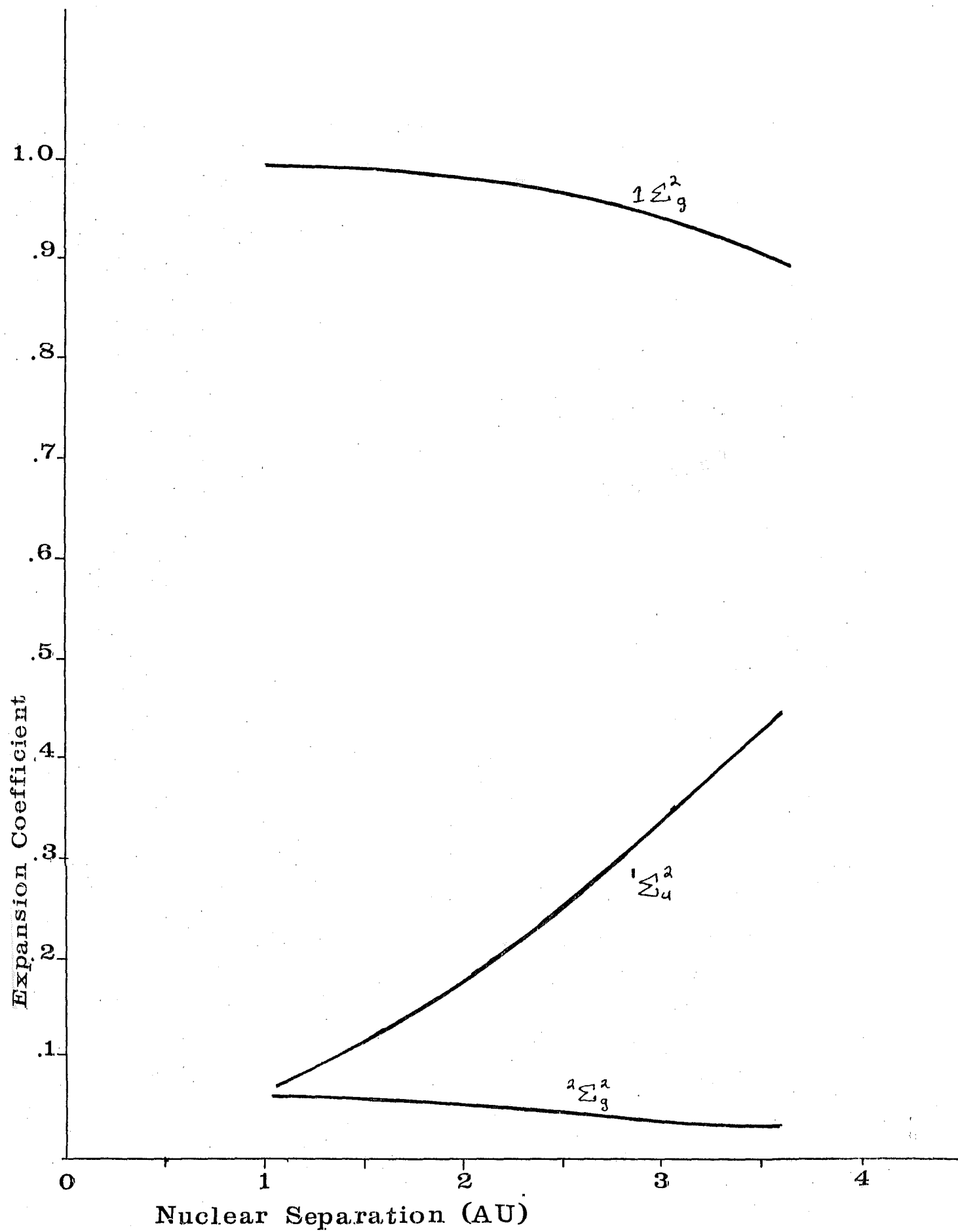
80	-.05069550			
		-.04900000		
98	-.05499658		-.04683095	
		-.06370627		-.03885508
116	-.05379500		-.04537302	
		-.05076600		
134	-.05053159			

Coefficient of  $(1\sigma_u)^2$ 

80	-.10608654			
		-.10557454		
98	-.10591728		-.10558711	
		-.10558109		-.10661511
116	-.10582180		-.10624503	
		-.10588797		
134	-.10583827			

$H_2$  TOTAL ENERGY  
FIG 4.1





## 5. TRANSCORRELATED HAMILTONIAN FOR DIATOMIC MOLECULES

### CORRELATION FUNCTIONS

The MCHF approximation provides one method of obtaining expectation values for a many electron system with an accuracy approaching experiment. However the effort involved is considerable. This is because the effort involved varies as  $n^2$  where  $n$  is the number of terms in the MCHF expansion. Any reduction in the number of terms required in the expansion is obviously worthwhile. This cannot be achieved using single particle spin orbitals since the basis set obtained from the solution of the MCHF equations is the best possible of this type.

The reason for the slow convergence when a basis set of single particle wavefunctions is used is the presence of a cusp in the wavefunction when the interelectron distance  $r_{ij}$  approaches zero. The problem has been likened to that of expanding a square wave in a Fourier series, a great many terms are necessary to represent the discontinuity in gradient.

If we consider the two-electron Schrödinger's equation as  $r_{12} \rightarrow 0$  (Slater 1960 [41]) the total wavefunction becomes asymptotic to  $\exp(\frac{1}{2} r_{12})$  i.e.

$$\left. \frac{1}{\psi} \frac{\partial \psi}{\partial r_{12}} \right|_{r_{12}=0} = \frac{1}{2} \quad (5.1)$$

which is the cusp condition (Roothaan and Weiss 1960).

This cusp condition makes for rather slow convergence when only single particle functions are used as a basis set, since we are expanding a function with points of discontinuity in gradient in terms of functions which are everywhere smooth.

Hylleraas (1929) was the first to exploit the use of a basis set containing  $r_{ij}$  explicitly. His calculations on He [27] demonstrated the greatly improved rates of convergence possible when  $r_{12}$  is included in the basis set.

Unfortunately this type of basis set is restricted to small systems, notably He,  $H_2$  and in a simplified form Li, as the effort required to evaluate multidimensional integrals soon exceeds the capabilities of today's computer.

Boys and Handy [11] have introduced a method which overcomes many of the problems of MCHF and Hylleraas type expansions, however it does introduce some new problems.

Boys and Handy introduce a new operator,  $C^{-1}HC$ , where  $H$  is the Hamiltonian of the system and  $C$  is some correlation function dependent on the interelectron distance.

We exploit the following properties of  $C^{-1}HC$  operator:

- (a)  $C^{-1}HC$  has the same eigenvalue spectrum as  $H$ ;
- (b) if  $C \equiv \prod_{i \neq j} e^{\frac{1}{2}r_{ij}}$  then  $C^{-1}HC$  is free of singularities at  $r_{ij} = 0$ ;
- (c) no integrals greater than nine dimensional occur in matrix elements of  $C^{-1}HC$ ; and

(d) as a consequence of (b) multiconfiguration expansions (if they are necessary) should be considerably shorter than a MCHF expansion to give a comparable accuracy.

The disadvantage of the method is that the  $C^{-1}HC$  operator is non-Hermitian. Thus, traditional variational methods cannot be used to obtain upper bounds to the eigenvalues of this operator.

#### THE TRANSCORRELATED OPERATOR - $C^{-1}HC$ .

We will consider a N electron system with Hamiltonian

$$H = \sum_{i=1}^N (-\frac{1}{2}\nabla_i^2 + V(r_i)) + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{r_{ij}} \quad (5.2)$$

and assume that a good approximation to the wavefunction of the system can be written as

$$\Psi^e = C\Psi \quad (5.3)$$

where C is a correlation function (containing non-separable functions of  $r_{ij}$   $i, j = 1, N$ ) and  $\psi$  is a sum of Slater determinants of single particle spin-orbitals.

We may now write

$$\langle H \rangle = \frac{\langle C\Psi | H | C\Psi \rangle}{\langle C\Psi | C\Psi \rangle} \quad (5.4)$$

In evaluating (5.4) we are faced with the problem of evaluating 3N dimensional integrals which is not feasible.

If  $C\Psi$  were an exact wavefunction then we could replace (5.4) by

$$E = \langle H \rangle = \frac{\langle f(\underline{r}_1 \underline{r}_2 \cdots \underline{r}_N) | H | C\Psi \rangle}{\langle f(\underline{r}_1 \cdots \underline{r}_N) | C\Psi \rangle}$$

assuming  $C\Psi$  is normalised and  $f$  is sufficiently well behaved.

When  $C\Psi$  is not an exact wavefunction we might expect  $\langle f | H | C\Psi \rangle$  to give a close approximation to  $\langle H \rangle$ , if  $C\Psi$  is a good approximation to the true wavefunction. Szondy [28] has considered approximations of this type and gives the technique the title 'The Method of Moments'. Boys and Handy have developed this idea in a series of papers [11]. By choosing  $f = C^{-1}\Psi$  the dimension of the integrals in  $\langle f | H | C\Psi \rangle$  is reduced, and no longer depends on  $N$ . Boys [29] has also used perturbation theory to show the error in  $\langle H \rangle$  can be expressed as a power series in  $\mu\mu^+$ , where  $\mu$  and  $\mu^+$  represent the errors in  $C\Psi$  and  $C^{-1}\Psi$  respectively.

So providing  $\mu$  is small we may expect  $\langle C^{-1}\Psi | H | C\Psi \rangle$  to provide a close approximation to  $\langle H \rangle$  even though  $\mu^+$  may be large.

Results of calculations on some atomic and molecular systems by Boys and Handy [11],[42] suggest this method of approach may be a fruitful one.

Fimple and Unwin [30] using a modification of the methods of Boys and Handy, have also obtained encouraging results for the Helium atom. Armour has obtained comparable results for  $H_2$  [31],[43]. The author has used the same

approach as Fimple and Unwin and it will be considered in detail in the next section.

It should be noted that  $\langle C^{-1}\psi | H | C\psi \rangle$  may be rewritten as  $\langle \psi | C^{-1}HC | \psi \rangle$  and the problem regarded as one of finding approximate eigenvalues and eigenfunctions of the new operator  $C^{-1}HC$  which has the same eigenvalue spectrum as  $H$ .

When a correlation function of the form

$$C = \prod_{i>j} \exp(f_{ij})$$

is chosen then  $C^{-1}HC$  consists only of one, two, and three electron operations.

$$C^{-1}HC = \sum_{i=1}^N F_i + \sum_{i \neq j=1}^N F_{ij} + \sum_{i \neq j \neq k} F_{ijk}$$

where

$$F_i = -\frac{1}{2}\nabla_i^2 + V(r_i) \quad (5.5)$$

$$F_{ij} = \frac{1}{2} \frac{1}{r_{ij}} - \frac{1}{2} \frac{\nabla_i^2 f_{ij}}{f_{ij}} - \frac{\nabla_i f_{ij} \cdot \nabla_i}{f_{ij}} \quad (5.6)$$

$$F_{ijk} = -\frac{1}{2} \frac{\nabla_i f_{ij} \cdot \nabla_i f_{ik}}{f_{ij} f_{ik}} \quad (5.7)$$

Note that  $C^{-1}HC$  is non-Hermitian, and it is the  $\frac{\nabla_i f_{ij} \cdot \nabla_i}{f_{ij}}$  term in (5.6) which is non-Hermitian. To demonstrate this we consider



$$\begin{aligned}
& \int g^*(r_1) \left| \frac{-\nabla_1 f_{12} \cdot \nabla_1}{f_{12}} \right| h(r_1) dr_1 \\
&= \int g^*(r_1) \left| \frac{1}{f_{12}} \left( \frac{\partial f_{12}}{\partial x_1} \frac{\partial}{\partial x_1} + \frac{\partial f_{12}}{\partial y_1} \frac{\partial}{\partial y_1} + \frac{\partial f_{12}}{\partial z_1} \frac{\partial}{\partial z_1} \right) \right| h(r_1) dr_1 .
\end{aligned} \tag{5.8}$$

Evaluating this by parts we have

$$\int h(r) \left| \frac{\nabla_1 f_{12} \cdot \nabla_1}{f_{12}} - \left( \frac{\nabla_1 f_{12}}{f_{12}} \right)^2 + \frac{\nabla_1^2 f_{12}}{f_{12}} \right| g^*(r_1) dr_1 , \tag{5.9}$$

and thus

$$F_{ij}^\dagger = \frac{1}{2} \frac{1}{r_{12}} + \frac{1}{2} \frac{\nabla_i^2 f_{ij}}{f_{ij}} + \frac{\nabla_i f_{ij} \cdot \nabla_i}{f_{ij}} - \left( \frac{\nabla_i f_{ij}}{f_{ij}} \right)^2 \tag{5.10}$$

which will not normally be equal to  $F_{ij}$ .

#### A VARIATIONAL METHOD FOR NON-HERMITIAN OPERATORS.

We will consider finding approximate solutions to the eigenvalue equation

$$\begin{aligned}
O\psi &= \lambda\psi \\
\chi O &= \lambda^*\chi
\end{aligned} \tag{5.11}$$

where  $O$  is an operator not necessarily Hermitian and  $\psi$  and  $\chi$  are its right and left hand eigenfunctions respectively.

It can be shown (Morse and Feshbach [33]) that the expectation value of any linear operator is stationary w.r.t. small independent variations of its left and right hand eigenfunctions subject to a normalisation constraint.

$$\left. \begin{aligned}
\langle \chi + \delta\chi | O | \psi \rangle &= 0 \\
\langle \chi | O | \psi + \delta\psi \rangle &= 0
\end{aligned} \right\} \tag{5.12}$$

$$\langle \chi + \delta\chi | \psi + \delta\psi \rangle = 1$$

So, by considering the inner product,

$$\langle \psi^L | 0 | \psi^R \rangle \quad (5.13)$$

and finding stationary values w.r.t. independent variations of the left and right trial functions then the resulting bra and ket will (providing sufficiently flexible trial functions are used) be good approximations to the eigenfunctions of 0.

Applying this procedure to  $C^{-1}HC$  we demand

$$\left. \begin{aligned} \langle \delta \psi^L | C^{-1}HC - E | \psi^R \rangle &= 0 \\ \langle \psi^L | C^{-1}HC - E | \delta \psi^R \rangle &= 0 \\ \langle \psi^L | \psi^R \rangle &= 1 \end{aligned} \right\} \quad (5.14)$$

While solution of these equations will not give an upper bound on  $E$ , Boys [29] has shown that if an analytic basis set is used then the eigenvalues and eigenvectors obtained converge to the correct values as the trial space is extended. This is equivalent to increasing the flexibility of the trial functions  $\psi^L$  and  $\psi^R$ .

Equations (5.14) will be referred to as the bivariational equations.

MULTICONFIGURATION BIVARIATIONAL EQUATIONS FOR DIATOMIC MOLECULES.

In this section the same form for  $\psi^L$  and  $\psi^R$  is chosen as for the MCHF equations (4.1) i.e.

$$\psi^L = \sum_I a_I \psi_I^L \quad (5.15)$$

$$\psi^R = \sum_I b_I \psi_I^R$$

Using (5.5 - 5.7) and (5.15) we may express (5.14) as

$$\begin{aligned} \delta (\langle \psi^L | C^{-1} H C | \psi^R \rangle - \sum_{\alpha, \beta} \sum_{IJ} \lambda_{\alpha\beta}^{IJ} \langle \phi_{I\alpha}^L | \phi_{J\beta}^R \rangle) \\ - \sum_{\alpha} \sum_I \mu_{\alpha}^I \langle \phi_{\alpha}^I | \phi_{\alpha}^I \rangle - E \langle \psi^L | \psi^R \rangle = 0 \end{aligned} \quad (5.16)$$

$\lambda_{\alpha\beta}^{IJ}$ ,  $\mu_{\alpha}^I$  and  $E$  are Lagrange multipliers associated with

$$\begin{aligned} \langle \phi_{I\alpha}^L | \phi_{I\beta}^R \rangle &= \delta_{\alpha\beta} & \alpha, \beta &= 1, N \\ & & I, J &= 1, M \\ \langle \phi_{\alpha}^I | \phi_{\alpha}^I \rangle &= 1 & \alpha, \beta &= 1, N \end{aligned} \quad (5.17)$$

$$\langle \psi^L | \psi^R \rangle = \sum_I a_I b_I = 1$$

$\mu_{\alpha}^I$  is included only to ensure stability in the numerical solution (5.16). It can be shown to be zero when (5.16) is satisfied.

Considering independant variations of

$$\phi_{I\alpha}^L \text{ and } \phi_{I\alpha}^R \quad I = 1, M, \quad \alpha = 1, N$$

a set of  $2MN$  coupled integro-differential equations results. These equations are similar to the MCHF equations and the method of solution is the same.

We have

$$\begin{aligned} a_I \sum_{J=1}^M b_J [ (F_1 + Y_{\alpha}^{IJ}(1)) \phi_{\alpha}^J(1) - X_{\alpha}^{IJ}(1) + Z_{\alpha}^{IJ}(1) \\ - \sum_{\beta} \lambda_{\alpha\beta}^{IJ} \phi_{\beta}^J(1) ] = 0 \quad \alpha = 1, \dots N \\ I = 1, \dots M \end{aligned} \quad (5.18)$$

$$\begin{aligned} b_I \sum_{J=1}^M a_J [ (F_1 + Y_{\alpha}^{IJ}(1)) \phi_{\alpha}^J(1) - X_{\alpha}^{IJ}(1) + Z_{\alpha}^{IJ}(1) \\ - \sum_{\beta} \lambda_{\alpha\beta}^{IJ} \phi_{\beta}^J(1) - 2\mu_{\alpha}^I \phi_{\alpha}^I(1) ] = 0 \end{aligned} \quad (5.19)$$

where

$$\left. \begin{aligned} Y_{\alpha}^{IJ}(1) &= \sum_{\beta} \langle \phi_{\beta}^I(2) | F_{12} + F_{21} | \phi_{\beta}^J(2) \rangle \\ X_{\alpha}^{IJ}(1) &= \sum_{\beta} \phi_{\beta}^J \langle \phi_{\beta}^I(2) | F_{12} + F_{21} | \phi_{\beta}^J(2) \rangle \\ Z_{\alpha}^{IJ}(1) &\equiv 3! \sum_{\substack{\beta, \gamma \\ \neq \alpha}}^{\dagger} \langle \phi_{\beta}^I(2) \phi_{\gamma}^J(3) | F_{123} + F_{231} + F_{312} | \\ &\quad P_3^{(A)} \phi_{\alpha}^J(1) \phi_{\beta}^J(2) \phi_{\gamma}^J(3) \rangle \end{aligned} \right\} \quad (5.20)$$

$$Y_{\alpha}^{IJ} = \sum_{\beta} \langle \phi_{\beta}^I(2) | F_{12}^{\dagger} + F_{21}^{\dagger} | \phi_{\beta}^J(2) \rangle$$

where  $P_3^{(A)}$  is the antisymmetric projector of the spin-orbitals  $\phi_{\alpha}^J(1) \phi_{\beta}^J(2) \phi_{\gamma}^J(3)$ .

$$X^{IJ} = \sum_{\beta} \phi_{\beta}^J(1) \langle \phi_{\beta}^I(2) | F_{12}^{\dagger} + F_{21}^{\dagger} | \phi_{\alpha}^J(2) \rangle \quad (5.21)$$

$$Z^{IJ} = 3! \sum_{\substack{\beta, \gamma \\ \neq \alpha}} \langle \phi_{\beta}^I(2) \phi_{\gamma}^I(3) | F_{123} + F_{231} + F_{312} | P_3^{(A)} \phi_{\alpha}^J(1) \phi_{\beta}^J(2) \phi_{\gamma}^J(3) \rangle$$

Varying the  $a_I$ 's and  $b_I$ 's results in two matrix eigenvalue equations.

$$\sum_I a_I (\langle \psi_I^L | C^{-1} H C | \psi_I^R \rangle - E) = 0 \quad (5.22)$$

$$\sum_I (\langle \psi_I^L | C^{-1} H C | \psi_I^R \rangle - E) b_I = 0$$

A direct solution of these equations was not attempted although it is quite possible using the same methods as were used in the solution of the MCHF equations.

A solution to the single configuration case was obtained using the coupled SCF-FDNRA method described in Chapter III, results are presented in Table (5.2). Approximations to the excited configurations were obtained from solutions to the MCHF equations given in Chapter III, they were of the form

$$\psi_I^L = e^{p\lambda} \psi_I \text{ (MCHF)} \quad (5.23)$$

$$\psi_I^R = e^{-p\lambda} \psi_I \text{ (MCHF)}$$

where  $p$  was obtained by minimizing

$$\int (e^{-p\lambda} \psi_1(\text{MCHF}) - \psi_R^R)^2 d\lambda$$

### THE $1\sum_g^+$ GROUND STATE OF $H_2$

Rewriting equations (5.18) and (5.19) for a single  $1\sigma_g^2$  configuration and assuming

$$\phi^L = L^L(\lambda) M^L(\mu)$$

$$\phi^R = L^R(\lambda) M^R(\mu)$$

we have

$$\left(\frac{\partial}{\partial \lambda}(\lambda^2 - 1)\frac{\partial}{\partial \lambda} + 2R\lambda + F(\lambda) + p^2\lambda^2 + A_1\right)L^R(\lambda) = 0 \quad (5.24a)$$

$$\left(\frac{\partial}{\partial \mu}(1 - \mu^2)\frac{\partial}{\partial \mu} - A_2 + G(\mu) - p^2\mu^2\right)M^R(\mu) = 0 \quad (5.24b)$$

$$\left(\frac{\partial}{\partial \lambda}(\lambda^2 - 1)\frac{\partial}{\partial \lambda} + 2R\lambda + F'(\lambda) + p^2\lambda^2 + A_1'\right)L^L(\lambda) - 2\Lambda H(\lambda)L^R(\lambda) = 0 \quad (5.24c)$$

$$\left(\frac{\partial}{\partial \mu}(1 - \mu^2)\frac{\partial}{\partial \mu} - A_2' + G'(\mu) - p^2\mu^2\right)M^L(\mu) - 2\Lambda J(\mu)M^R(\mu) = 0 \quad (5.24d)$$

where

$$F(\lambda) = \frac{-R^5}{16} \int (\lambda^2 - \mu^2) M^L(\mu) Y_\alpha(\lambda, \mu, \phi) M^R(\mu) d_\mu d\phi / \int M^L M^R d_\mu$$

$$A_1 = \int M^L \left( \frac{\partial}{\partial \mu}(1 - \mu^2)\frac{\partial}{\partial \mu} - p^2\mu^2 \right) M^R d_\mu / \int M^L M^R d_\mu$$

$$G(\mu) = \frac{-R^5}{16} \int (\lambda^2 - \mu^2) L^L(\lambda) Y_\alpha(\lambda, \mu, \phi) L^R(\lambda) d\lambda d\phi / \int L^L L^R d\lambda$$

$$A_2 = \int L^L \left( \frac{\partial}{\partial \lambda}(\lambda^2 - 1)\frac{\partial}{\partial \lambda} + 2R\lambda + p^2\lambda^2 \right) L^R d\lambda d\phi / \int L^L L^R d\lambda \quad (5.25)$$

$$F'(\lambda) = \frac{-R^5}{16} \int (\lambda^2 - \mu^2) M^R(\mu) Y'_\alpha(1) M^R(\mu) d\mu d\phi / \int M^L M^R d\mu$$

$A_1^I = A_1$  from integration by parts

$$A_2^I = A_2$$

$$G'(\mu) = \frac{-R^5}{16} \int (\lambda^2 - \mu^2) L^R(\lambda) Y'_\alpha(1) L^L(\lambda) d\phi d\lambda / \int L^L L^R d\lambda$$

$$H(\lambda) = \int (\lambda^2 - \mu^2) M^L M^R d\mu$$

(5.26)

$$J(\mu) = \int (\lambda^2 - \mu^2) L^L L^R d\lambda$$

$F(\lambda), F'(\lambda), G(\mu), G'(\mu)$  may be expressed as

$$F(\lambda) = F_1(\lambda_1) \frac{\partial}{\partial \lambda_1} + F_2(\lambda_1)$$

$$F'(\lambda) = F_1^I(\lambda) \frac{\partial}{\partial \lambda_1} + F_2^I(\lambda_1)$$

(5.27)

$$G(\mu) = G_1(\mu) \frac{\partial}{\partial \mu_1} + G_2(\mu)$$

$$G'(\mu) = G_1^I(\mu) \frac{\partial}{\partial \mu} + G_2(\mu)$$

Equations (5.27) are expressed more fully in confocal elliptical coordinates in appendix B.

Finally we make the transformations (2.10-2.13) to arrive at a form of (5.24) suitable for solution using FDNRA. (5.24) becomes

$$\begin{aligned}
& [B_1(\zeta) \frac{d^2}{d\zeta^2} + (C_1(\zeta) + (1-b\zeta)^2 F_1(\zeta)) \frac{d}{d\zeta} - \frac{2(1+(1-b)\zeta)}{2\zeta+(1+2b)\zeta^2} F_1(\zeta) \\
& + F_2(\zeta) + D_1(\zeta) + A - \frac{p^2(1+(1-b)\zeta)^2}{(1-b\zeta)^2}] X^R(\zeta) = 0 \quad (5.28a)
\end{aligned}$$

$$\begin{aligned}
& [B_2(\rho) \frac{d^2}{d\rho^2} + (C_2(\rho) + \frac{(2-2(1+4A\rho^2)^{\frac{1}{2}}+4A\rho^2)}{2\rho^2(1-(1+4A\rho^2)^{\frac{1}{2}}+4A\rho^2)} G_1(\rho)) \frac{d}{d\rho} \\
& + \frac{\rho(-1+(1+4A\rho^2)^{\frac{1}{2}})}{2\rho^2-1+2A\rho^2+(1+4A\rho^2)} G_1(\rho) + G_2(\rho) + D_2(\rho) - A + \frac{p^2(\sqrt{1+4A\rho^2}-1)}{8\rho^2}] Y^R(\rho) \\
& = 0 \quad (5.28b)
\end{aligned}$$

$$\begin{aligned}
& [B_1(\zeta) \frac{d^2}{d\zeta^2} + (C_1(\zeta) + (1-b\zeta)^2 F_1(\zeta)) \frac{d}{d\zeta} - \frac{2(1+(1-b)\zeta)}{2\zeta+(1+2b)\zeta^2} F_1(\zeta) \\
& + F_2(\zeta) + D_1(\zeta) + A - \frac{p^2(1+(1-b)\zeta)^2}{(1-b\zeta)^2}] X^L(\zeta) - 2\Lambda H(\zeta) X^R(\zeta) = 0 \quad (5.28c)
\end{aligned}$$

$$\begin{aligned}
& [B_2(\rho) \frac{d^2}{d\rho^2} + (C_2(\rho) + \frac{(2-2(1+4A\rho^2)^{\frac{1}{2}}+4A\rho^2)}{2\rho^2(1-(1+4A\rho^2)^{\frac{1}{2}}+4A\rho^2)} \frac{d}{d\rho} \\
& + \frac{\rho(-1+(1+4A\rho^2)^{\frac{1}{2}})}{2\rho^2-1+2A\rho^2+(1+4A\rho^2)} G_1(\rho) + G_2(\rho) + D_2(\rho) \\
& - A + \frac{p^2(\sqrt{1+4A\rho^2}-1)}{8\rho^2}] Y^L(\rho) - 2\Lambda J(\rho) Y^R(\rho) = 0 \quad (5.28d)
\end{aligned}$$

By premultiplying (5.24a) by  $L^L(\lambda)$  and integrating over  $\lambda$  an equation relating  $A_1$  and  $A_2$  of equations (5.25) is obtained

$$A_2 - A_1 = \int L^L(\lambda) [F_1(\lambda) \frac{d}{d\lambda} + F_2(\lambda)] L^R(\lambda) d\lambda / \int L^L(\lambda) L^R(\lambda) d\lambda \quad (5.29)$$

Including normalisation constraints



$$\begin{aligned} & \frac{R^3}{8} \int X^L(\zeta) X^R(\zeta) Y^L(\rho) Y^R(\rho) \frac{(-1+(4A\rho^2+1)^{\frac{1}{2}})}{(1+4A\rho^2)(2\rho^2(1-A)-1+2(1+4A\rho^2))^{\frac{1}{2}}} \\ & \cdot \frac{(1-b\zeta)^2}{\zeta^2(2(1-b)+\zeta)} \cdot \left( \frac{(1+(1-b)\zeta)^2}{1-b\zeta} - \frac{(-1+(1+4A\rho^2)^{\frac{1}{2}})^2}{4\rho^2} \right) d\rho d\zeta - 1 = 0 \end{aligned} \quad (5.30a)$$

$$\int Y^L(\rho) Y^R(\rho) \frac{(-1+(4A\rho^2+1)^{\frac{1}{2}}) d\rho}{(1+4A\rho^2)(2\rho^2(1-A)-1+2(1+4A\rho^2))} - 1 = 0 \quad (5.30b)$$

$$\int X^R(\zeta) X^L(\zeta) \frac{1}{(1-b\zeta)^2} d\zeta - 1 = 0$$

we have a set of equations (5.28, 5.29, 5.30) which may be solved using similar methods to those described in Chapter III for the HF problem.

#### METHOD OF SOLUTION

Revising the notation of Chapter II slightly we write

$$x_i^R = x^R(\zeta_i)$$

$$x_i^L = x^L(\zeta_i)$$

$$y_{j+N_1-1}^R = y^R(\rho_j)$$

$$y_{j+N_1-1}^L = y^L(\rho_j) \quad (5.31)$$

$$\zeta_i = kh_i$$

$$\rho_j = -1/(a-1) + jh_2$$

Using approximations (2.18-2.19) to the derivatives in (5.28-5.30) these equations are translated into a set of simultaneous algebraic equations.

For example (5.28a) becomes

$$B_1(\zeta_i)(X_{i+1} - 2X_i + X_{i-1})/h_i^2 + (C_1(\zeta_i) + (1-b\zeta_i)^2 F_1(\zeta_i))(X_{i+1} - X_{i-1})/2/h_i + \frac{(2(1+(1-b)\zeta_i))}{2\zeta_i + (1+2b)\zeta_i^2} F_1(\zeta_i) + F_2(\zeta_i) + D_1(\zeta_i) X_i = 0 \quad (5.32)$$

Similarly equations (5.28b,c,d 5.29 5.30) can be written in terms of the finite difference variables  $X_i^L$ ,  $X_i^R$ ,  $Y_j^L$ ,  $Y_j^R$ ,  $A_1$ ,  $\lambda_{11}$  and  $\Lambda$ .

As with the HF equations (3.4a & 3.4b) equations (5.32) are solved using a combined SCF NR iteration. When terms within the integrals (5.26-5.27) held constant equations (5.32) may be arranged in a form suitable for solution using the GNRI described in Chapter 2.

The strategy for solution is

- (1) Set  $\alpha = 0$  in the correlation function. Equations (5.32) are now the HF equations and are solved in the same manner.
- (2) Increment  $\alpha$  by a small amount ( $\approx .1$ ) calculate all integrals required using HF wavefunctions and solve (5.32)

using GNRI.

(3) Re-evaluate integrals and solve equations again.

Continue this process until results from one step to the next differ by less than a tolerance.

(4)  $\alpha$  may now be increased and step (3) repeated.

When  $\alpha = .5$  the equations are solved the single configuration  $C^{-1}HC$  equations it remains to calculate the energy and expansion coefficients for a CI type expansion using the excited MCHF wavefunctions and the ground state  $C^{-1}HC$  wavefunctions. Fimple and Unwin (30) describe an efficient algorithm for the non-homogeneous eigenvalue problem which results from the CI for  $C^{-1}HC$ .

## RESULTS

Again we present an extrapolation of the total energy of the ground state at equilibrium distance (1.4 a.u.), in Table (5.1). Extrapolations for the expansion coefficients are also given.

We note that the total energy is somewhat improved over that of the FD-MCHF results with a shorter expansion.

Table 5.1:

No. Mesh Points	Total Energy		
80	-1.1682474E+00	-1.1747224E+00	
98	-1.1685695E+00	-1.1721841E+00	-1.1714271E+00
116	-1.1690807E+00		
Coefficient $1\sigma_g^2$			
80	9.6762458E-01		
98	9.6758115E-01	9.6770968E-01	9.6758001E-01
116	9.6756901E-01	9.6760930E-01	
Coefficient $2\sigma_u^2$			
80	1.3644202E-01		
98	1.3696335E-01	1.3721666E-01	1.3769730E-01
116	1.3721561E-01	1.3758689E-01	
Coefficient $1\pi_u^2$			
80	2.1089369E-01		
98	2.1178545E-01	2.1006958E-01	2.1217910E-01
116	2.1208949E-01	2.1169450E-01	

## 6. CONCLUSIONS

The coupled FDNRA-SCF iteration technique is a powerful tool in calculating approximate solutions to Schrödingers equation for diatomic molecules.

As the differential equations resulting from various approximations to the solution of Schrödingers equation are solved directly rather than by using a basis set expansion there is no concern over choosing a basis set which will adequately represent the solution of these differential equations.

It is felt, that of the approximations considered in this thesis, the  $C^{-1}HC$  approximation would be the most fruitful direction for further investigation. The results obtained even with the rather simple correlation function choosen were better than those obtained for MCHF with a shorter expansion.

There are two directions this research could take.

(1) Retain the present simple correlation function  $\sum_{i \neq j} e^{\frac{1}{2}r_{ij}}$  and use a full MC- $C^{-1}HC$  expansion.

Work by the author on  $H_2$  and Fimple and Unwin [30] on He suggests that there is no need to include excited  $\sigma_g^2$  ( $s^2$  atomic) states in the expansion, at least in the cases studied. This may not remain true for larger systems.

(2) A more complicated correlation function, could be used. One disadvantage of the correlation function used

in this work is that it is not bounded. It has the correct asymptotic behaviour as  $r_{12} \rightarrow 0$  but not as  $r_{12} \rightarrow \infty$ . An improvement would be a correlation function with the following properties,

$$(i) \quad \left. \frac{dC}{dr_{12}} \right|_{r_{12}=0} = \frac{1}{2}$$

$$(ii) \quad \lim_{r_{12} \rightarrow \infty} C(r_{12}) = \text{Constant}$$

$$(iii) \quad C = \exp(f(r_{12})).$$

The correlation function used in this work satisfies all but ii. A simplification of the correlation function of Boys and Handy [11] will satisfy all three requirements, i.e.  $C = \prod_{ij} \exp(\rho_{ij})$  where  $\rho_{ij} = \frac{r_{ij}}{1+ar_{ij}}$   $a > 0$ . With the methods described in this thesis there is no need for the redundant parameters normally included in such a correlation function. Nor is it necessary to include the adjustable parameter  $a$ , since providing the trial wavefunction is flexible enough calculated energies should be independent of  $a$ . This may well give an indication of when sufficient terms have been included in a MC expansion.

It is the author's opinion that investigation of such a correlation function using the FDNRA methods described in this thesis would be well rewarded.

The present thesis has provided a new tool for the further investigation of the structure of diatomic molecules.

ACKNOWLEDGEMENTS

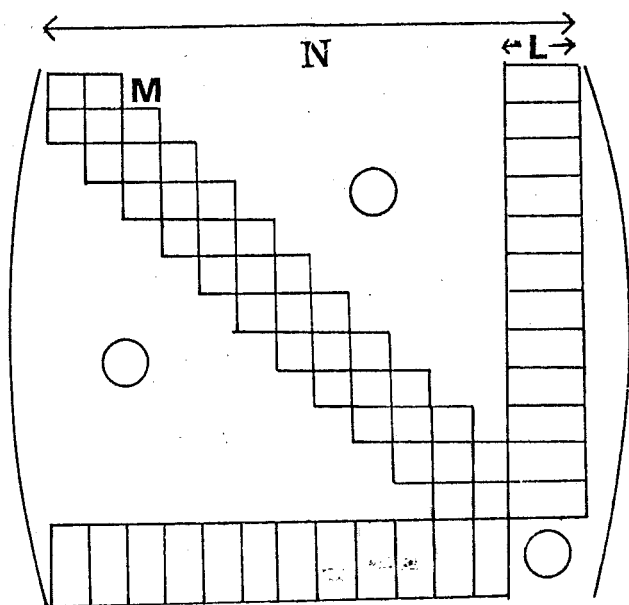
The author wishes to thank Dr Bill Fimple for all his assistance, encouragement, and advice during the course of this work.

Thanks are also extended to Dr Joel Cayford, Martin Unwin and Dr Mike Moy for the many stimulating discussions and ideas which helped with this work. Finally I wish to thank the Physics Department of the University of Canterbury for financial assistance throughout this work, and the NZPO for assistance in its publication.

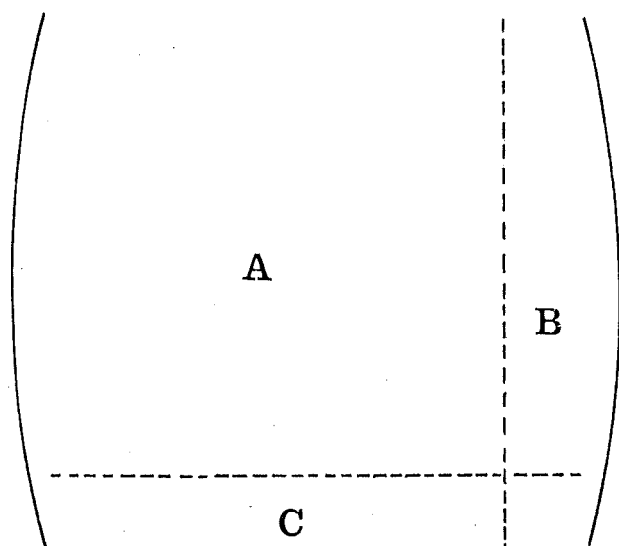
# APPENDIX A

## RAPID INVERSION OF SPARSE MATRICES

The Jacobian matrices encountered in this work have all been special cases of the following matrix.



By partitioning this matrix into a  $(N-L) \times (N-L)$  block tri-diagonal matrix a  $L \times (N-L)$  and  $(N-L) \times L$  matrices inversion time can be very much reduced. We partition it as follows.





We write the N.R. iteration as

$$Z^{i+1} = Z^i - J^{-1} F^i \quad (A1)$$

which may be written as

$$J \underline{\Delta} = F^i \quad (A2)$$

where

$$\underline{\Delta} = Z^i - Z^{i+1}$$

writing  $\underline{\Delta} = \begin{pmatrix} \Delta_1 \\ \Delta_2 \end{pmatrix}$  and  $F^i = \begin{pmatrix} F_1^i \\ F_2^i \end{pmatrix}$  where  $\Delta_1$  and  $F_1^i$  are vectors of length  $N-L$  and  $\Delta_2$  and  $F_2^i$  are vectors of length  $L$

A2 becomes

$$\begin{pmatrix} A & B \\ C & O \end{pmatrix} \begin{pmatrix} \Delta_1 \\ \Delta_2 \end{pmatrix} = \begin{pmatrix} F_1 \\ F_2 \end{pmatrix} \quad (A3)$$

$$A\Delta_1 + B\Delta_2 = F_1 \quad (A4)$$

$$C\Delta_1 = F_2 \quad (A5)$$

premultiplying A4 by  $CA^{-1}$  and using A5 gives

$$CA^{-1}B\Delta_2 = CA^{-1}F_1 - F_2 \quad (A6)$$

and rearranging A4 gives

$$A\Delta_1 = F_1 - B\Delta_2 \quad (A7)$$

Equations (A6) and (A7) may be solved as follows.

We first obtain the matrix  $A^{-1}B$  by defining

$$\omega_1 \equiv A_{11}^{-1} A_{12}$$

$$\omega_j \equiv (A_{jj} - A_{jj-1} \omega_{j-1})^{-1} A_{jj+1}$$

$$G_{1k} \equiv A_{11}^{-1} B_{1k} \quad G_{jk} \equiv (A_{jj} - A_{jj-1} \omega_{j-1})^{-1} \cdot (B_{jk} - A_{jj-1} G_{j-1,k})$$

from which the elements of  $A^{-1}B$  may be computed recursively.

$$(A^{-1}B)_{N*M-L,K} = G_{N*M-L,K}$$

$$(A^{-1}B)_{jk} = G_{jk} - \omega_j (A^{-1}B)_{j+1,k} \quad \begin{array}{l} j = N-L-1, \dots, 1 \\ k = 1, \dots, L \end{array}$$

Similarly we obtain  $A^{-1}F_1$ . Inversion of the  $L \times L$  matrix  $CA^{-1}B$  and multiplying (A6) through by  $(CA^{-1}B)^{-1}$  gives  $\Delta_2$ .

Using the same method as used to obtain  $A^{-1}B$  we obtain  $\Delta_1 = A^{-1} (F_1 - B\Delta_1)$  and the inversion is complete.

## APPENDIX B

### A TECHNIQUE FOR THE EVALUATION OF SOME MOLECULAR INTEGRALS

Numerical integration over more than one dimension is a very time consuming process. For the methods discussed in this thesis to be of value an efficient method of evaluating integrals of the form

$$B_{\alpha}(\lambda) = \frac{R^5}{64\pi^2} \sum_{\beta \neq \alpha} \int \frac{M_{\alpha}^2(\mu) M_{\beta}^2(\mu') L_{\beta}^2(\lambda') (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) d\tau}{r_{12}} \quad (B1)$$

$$d\tau = d\lambda' d\mu d\mu' d\phi d\phi'$$

$$r_{12} = |\bar{\mathbf{r}}_1 - \bar{\mathbf{r}}_2|$$

must be available.

A technique has been developed which may be used for all multidimensional integrals required for the present work and with a slight modification may also be used for integrals in similar calculations on atomic systems.

Taking a single term from the summation in (B1) we have

$$I_{\beta}(\lambda) = \int \frac{M_{\alpha}^2(\mu) M_{\beta}^2(\mu') L_{\beta}^2(\lambda') (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) d\tau}{r_{12}} \quad (B2)$$

Expanding  $\frac{1}{r_{12}}$  we have

$$\frac{1}{r_{12}} = \frac{2}{R} \sum_{k=0}^{\infty} (2k+1) \sum_{M=-k}^k (-1)^M \left| \frac{(k-|M|)!}{(k+|M|)!} \right|^2$$

$$\times P_k^{(|M|)}(\lambda_<) Q_k^{(|M|)}(\lambda_>) P_k^{(|M|)}(\mu) P_k^{(|M|)}(\mu') e^{iM(\phi-\phi')} \quad (B3)$$

where

$$\lambda_< = \min(\lambda, \lambda'), \quad \lambda_> = \max(\lambda, \lambda'),$$

and  $P_k^{(|M|)}$  and  $Q_k^{(|M|)}$  are associated Legendre functions of the first and second kind. Substituting (B3) into (B2)

$I_\beta(\lambda)$  becomes

$$I_\beta(\lambda) = \frac{8\pi^2}{R} \sum_{k=0}^{\infty} \int M_\alpha^2(\mu) M_\beta^2(\mu') L_\beta^2(\lambda') \cdot$$

$$\times P_k(\lambda_<) Q_k(\lambda_>) P_k(\mu) P_k(\mu') (\lambda^2 - \mu^2) (\lambda'^2 - \mu'^2) \cdot$$

$$\times d\lambda' d\mu d\mu' \quad (B4)$$

Note that in this case only the  $M = 0$  terms are non-zero and that the integrations over  $\phi$  and  $\phi'$  have been done analytically. The  $k$ th term of the series (B4) expands out to

$$I_{\beta k} = \lambda^2 \left[ \int \lambda'^2 L_\beta^2(\lambda') P_k(\lambda_<) Q_k(\lambda_>) d\lambda' \int M_\beta^2(\mu') P_k(\mu') d\mu \cdot \right.$$

$$\times \int M_\alpha^2(\mu) P_k(\mu) d\mu$$

$$\left. - \int L_\beta^2(\lambda') P_k(\lambda_<) Q_k(\lambda_>) d\lambda' \int M_\beta^2(\mu') \mu'^2 P_k(\mu') d\mu \cdot \right]$$

$$\begin{aligned}
& \times \int M_{\alpha}^2(\mu) P_K(\mu) d\mu] - \\
& \left[ \int L_{\beta}^2(\lambda') P_K(\lambda_{<}) Q_K(\lambda_{>}) d\lambda' \int M_{\beta}^2(\mu') P_K(\mu') d\mu \right. \\
& \times \int M_{\alpha}^2(\mu) \mu^2 P_K(\mu) d\mu - \\
& \left. \int L_{\beta}^2(\lambda') P_K(\lambda_{<}) Q_K(\lambda_{>}) \int M_{\beta}^2(\mu') P_K(\mu') \mu'^2 d\mu' \right. \\
& \times \left. \int \mu^2 M_{\alpha}^3(\mu) P_K(\mu) d\mu \right] . \tag{B5}
\end{aligned}$$

All the terms in (B5) are handled in the same manner so for simplicity we will just consider one,

$$\begin{aligned}
I'_{\beta K} &= \int L_{\beta}^2 P_K(\lambda_{<}) Q_K(\lambda_{>}) \int M_{\beta}^2(\mu') P_K(\mu') \mu'^2 d\mu' \\
&\times \int M_{\alpha}^2(\mu) P_K(\mu) d\mu . \tag{B6}
\end{aligned}$$

The integrations over  $\mu$  and  $\mu'$  are easily handled using conventional techniques, it was found that a Newton Coates order ten formula was most satisfactory. If lower order formulas (e.g. Simpsons Rule) are used results for large  $K$  may be in error. For homonuclear molecules all odd (or even) terms may be eliminated from the summation (B4) by symmetry considerations.

There remains the term

$$I''_{\beta K} = \int L_{\beta}^2(\lambda') P_K(\lambda_{<}) Q_K(\lambda_{>}) d\lambda' \tag{B7}$$

to be evaluated, the computer effort involved in this can be reduced to about the same as required for two one dimensional integrals.

Consider the  $\lambda$  axis to be broken into a series of points  $\lambda_0, \lambda_1, \dots, \lambda_N$  with  $L_\beta$  tabulated at each of these points with values  $L_0, L_1, \dots, L_N$ . At mesh point  $i$  (B7) becomes

$$\begin{aligned} I''_{\beta K}(\lambda_i) &= Q_K(\lambda_i) \int_1^{\lambda_i} L_\beta^2(\lambda') P_K(\lambda') d\lambda' \\ &+ P_K(\lambda_i) \int_{\lambda_i}^{\infty} L_\beta^2(\lambda') Q_K(\lambda') d\lambda' \end{aligned} \quad (B8)$$

which in terms of trapazoidal rule summations is

$$\begin{aligned} I''_{\beta K}(\lambda_i) &= Q_K(\lambda_i) \left| \sum_{j=1}^{i-1} L_j^2 P_K(\lambda_j) + \frac{1}{2}(L_0^2 + L_i^2) P_K(\lambda_i) \right| \\ &+ P_K(\lambda_i) \left| \sum_{j=i+1}^N L_j^2 Q_K(\lambda_j) + \frac{1}{2} L_i^2 Q_K(\lambda_i) \right|. \end{aligned} \quad (B9)$$

Similarly at the  $i+1$ th mesh point,

$$\begin{aligned} I''_{\beta K}(\lambda_{i+1}) &= Q_K(\lambda_{i+1}) \left| \sum_{j=1}^i L_j^2 P_K(\lambda_j) + \frac{1}{2}(L_0^2 + L_{i+1}^2) P_K(\lambda_{i+1}) \right| \\ &+ P_K(\lambda_{i+1}) \left| \sum_{j=i+1}^N L_j^2 Q_K(\lambda_j) + \frac{1}{2} L_{i+1}^2 Q_K(\lambda_{i+1}) \right|. \end{aligned} \quad (B10)$$

Note  $L_0 = L_\beta(1)$  and is evaluated using the methods of appendix D. Writing  $I''_{\beta K}(\lambda_\ell) = Q_K(\lambda_\ell) I_1(\lambda_\ell) + P_K(\lambda_\ell) I_2(\lambda_\ell)$

and comparing (B9) with (B10) shows

$$I_1(\lambda_{i+1}) = Q_K(\lambda_{i+1}) [I_1(\lambda_i)/Q_K(\lambda_i) + \frac{1}{2}(L_i^2 P_K(\lambda_i) + L_{i+1}^2 P_K(\lambda_{i+1}))] \quad (B11)$$

and

$$I_2(\lambda_{i+1}) = P_K(\lambda_{i+1}) [I_2(\lambda_i)/P_K(\lambda_i) - \frac{1}{2}(L_i^2 Q_K(\lambda_i) + L_{i+1}^2 Q_K(\lambda_{i+1}))]. \quad (B12)$$

So having calculated  $I_1(\lambda_1)$  and  $I_2(\lambda_1)$  using trapazoidal rule integration  $I_1(\lambda_i)$  and  $I_2(\lambda_i)$   $i = 2, 3 \dots N$  may be calculated very quickly. The same method may be used for each term in (B5) and the results combined to give the required integral.

This technique has been tested with analytic wavefunctions and very good agreement with analytic results was found. The error introduced by truncating (B3) was investigated by considering various truncations for the  $H_2$  calculation.

If for a given mesh spacing we truncate (B3) to  $n$  even terms the remainder error is

$$R_n = \Delta_{n+1} \left( 1 + \frac{\Delta_{n+2}}{\Delta_{n+1}} + \frac{\Delta_{n+3}}{\Delta_{n+1}} + \dots \right) \quad (B13)$$

$\Delta_n$  represents the change in HF energy as the  $n$ th term is added to the series. It was found that  $(\Delta_{n+1}/\Delta_n) < \frac{1}{2}$

for  $n > 10$ . Since

$$\frac{\Delta_{n+K+1}}{\Delta_{n+1}} = \prod_{i=1}^K \frac{\Delta_{n+i+1}}{\Delta_{n+i}} < \left(\frac{1}{2}\right)^K \quad (\text{B14})$$

the series (B13) sums to less than the geometric series  $\sum_{K=0}^{\infty} \left(\frac{1}{2}\right)^K = 2$ . So the truncation error inherent in the HF energy given for  $\text{H}_2$  is less than  $2\Delta_{1,1} = 1.2 \times 10^{-9}$ .

Such extensive investigation into truncation error was not performed for other cases, the criteria chosen for truncating the series was that the inclusion of the last term should not change the calculated energy by more than  $1 \times 10^{-9}$ .



# APPENDIX C

## C<sup>-1</sup>HC IN CONFOCAL ELLIPTICAL COORDINATES

The Hamiltonian of a diatomic molecule may be written as

$$- \sum_i \left( \frac{1}{2} \nabla_i^2 + \frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \quad (C1)$$

choosing a simple correlation function

$$C = \prod_{i > j} f_{ij}$$

we have

$$C^{-1}HC = \sum_i F_i + \sum_{i \neq j} F_{ij} + \sum_{ijk} F_{ijk} \quad (C2)$$

where

$$\begin{aligned} F_i &= -\frac{1}{2} \nabla_i^2 - \frac{Z_A}{r_{Ai}} + \frac{Z_B}{r_{Bi}} \\ F_{ij} &= \frac{1}{2} \frac{1}{r_{ij}} - \frac{1}{2} \frac{\nabla_i^2 f_{ij}}{f_{ij}} - \frac{\nabla_i f_{ij} \cdot \nabla_i}{f_{ij}} \\ F_{ijk} &= -\frac{1}{2} \frac{\nabla f_{ij} \cdot \nabla_i f_{ik}}{f_{ij} f_{ik}} \end{aligned} \quad (C3)$$

choosing

$$f_{ij} = e^{\frac{1}{2} r_{ij}} = e^y$$

$$\frac{\nabla_1 f_{12}}{f_{12}} = \frac{1}{4} + \frac{1}{r_{12}}$$

$$\begin{aligned} \frac{\nabla_1 f_{12} \cdot \nabla_1}{f_{12}} &= \frac{(\underline{r}_1 - \underline{r}_2)}{2r_{12}} \cdot \underline{\nabla}_1 \\ &= \frac{1}{2r_{12}} (x_{1i} - x_{2i}) \frac{\partial}{\partial x_{1i}} \end{aligned}$$

we have

$$\frac{\partial}{\partial x} = \frac{-8}{R^3 (\lambda^2 - \mu^2)} \left| -\frac{R^2}{4} \lambda (\lambda^2 - 1)^{\frac{1}{2}} (1 - \mu^2)^{\frac{1}{2}} \cos \phi \frac{\partial}{\partial \lambda} \right.$$

$$+ \frac{R^2}{4} \mu (\lambda^2 - 1)^{\frac{1}{2}} (1 - \mu^2)^{\frac{1}{2}} \cos \phi \frac{\partial}{\partial \mu}$$

$$\left. + \frac{R^2}{4} \frac{(\lambda^2 - \mu^2)}{(\lambda^2 - 1)^{\frac{1}{2}} (1 - \mu^2)^{\frac{1}{2}}} \sin \phi \frac{\partial}{\partial \phi} \right|$$

$$\frac{\partial}{\partial y} = \frac{-8}{R^3 (\lambda^2 - \mu^2)} \left| \frac{-R^2}{4} \lambda (\lambda^2 - 1)^{\frac{1}{2}} (1 - \mu^2)^{\frac{1}{2}} \sin \phi \frac{\partial}{\partial \lambda} \right.$$

$$+ \frac{R^2}{4} \mu (\lambda^2 - 1)^{\frac{1}{2}} (1 - \mu^2)^{\frac{1}{2}} \sin \phi \frac{\partial}{\partial \mu} - \frac{(\lambda^2 - \mu^2)}{(\lambda^2 - 1)^{\frac{1}{2}} (1 - \mu^2)^{\frac{1}{2}}} \cos \phi \frac{\partial}{\partial \phi} \left| \right.$$

$$\frac{\partial}{\partial z} = \frac{-8}{R^3 (\lambda^2 - \mu^2)} \left| \frac{-R^2}{4} \mu (\lambda^2 - 1) \frac{\partial}{\partial \lambda} - \frac{R^2}{4} \lambda (1 - \mu^2) \frac{\partial}{\partial \mu} \right| \quad (C4)$$

so

$$\frac{\nabla_1 f_{12} \cdot \nabla_1}{f_{12}} =$$

$$\begin{aligned}
& \frac{1}{2r_{12}} \left\{ \left| \frac{(\lambda_1^2-1)(\lambda_1-\mu_1\lambda_2\mu_2)}{(\lambda_1^2-\mu_1^2)} - \frac{\lambda_1(\lambda_1^2-1)^2(1-\mu_1^2)^2(\lambda_2^2-1)^2(1-\mu_2^2)^2}{(\lambda_1^2-\mu_1^2)} \right. \right. \\
& \cdot \cos(\phi_1-\phi_2) \left| \frac{\partial}{\partial \lambda_1} \right. \\
& + \left| \frac{(1-\mu_1^2)}{(\lambda_1^2-\mu_1^2)} (\mu_1-\lambda_1\lambda_2\mu_2) + \frac{\mu_1(\lambda_1^2-1)^{\frac{1}{2}}(1-\mu_1^2)^{\frac{1}{2}}(\lambda_2^2-1)^{\frac{1}{2}}(1-\mu_2^2)^{\frac{1}{2}}}{(\lambda_1^2-\mu_1^2)} \cos(\phi_1-\phi_2) \right| \frac{\partial}{\partial \mu_1} \\
& \left. + \frac{(\lambda_2^2-1)^{\frac{1}{2}}(1-\mu_2^2)^{\frac{1}{2}}}{(\lambda_1^2-1)^{\frac{1}{2}}(1-\mu_1^2)^{\frac{1}{2}}} \sin(\phi_1-\phi_2) \frac{\partial}{\partial \phi_1} \right\} \quad (C5)
\end{aligned}$$

the  $\frac{\nabla_2 f_{12} \cdot \nabla_2}{f_{12}}$  is obtained by interchanging the indices in (A3.5). We may now write equations (5.27) explicitly.

$$\begin{aligned}
F_1(\lambda) &= \frac{R^5}{32} \left| \int M^L(\mu_1) M^L(\mu_2) L^L(\lambda_2) \frac{1}{r_{12}} [(\lambda_1^2-1)(\lambda_1-\mu_1\mu_2\lambda_2) \right. \\
&\quad \left. - \lambda_1 D(\lambda_1, \lambda_2, \mu_1, \mu_2)] (\lambda_2^2-\mu_2^2) M^R(\mu_1) M^R(\mu_2) L^R(\lambda_2) d\tau_1 \right. \\
F_2(\lambda) &= \frac{R^5}{32} \left| \int \int M^L(\mu_1) M^L(\mu_2) L^L(\lambda_2) \frac{1}{r_{12}} [(1-\mu_1^2)(\mu_1-\lambda_1\lambda_2\mu_2) + \mu_1 D(\lambda_1, \lambda_2, \mu_1, \mu_2) \right. \\
&\quad \left. M_2^R(\mu_2) \frac{\partial M_1^R(\mu_1)}{\partial \mu_1} L^R(\lambda_2) (\lambda_2^2-\mu_2^2) d\tau_1 \right| \\
&+ \left| \int M^L(\mu_1) M^L(\mu_2) L^L(\lambda_2) \frac{1}{r_{12}} [(\lambda_2^2-1)(\lambda_2-\mu_2\lambda_1\mu_1) - \lambda_2 D(\lambda_1, \lambda_2, \mu_1, \mu_2)] \right. \\
&\quad \left. (\lambda_1^2-\mu_1^2) M^R(\mu_1) M^R(\mu_2) \frac{\partial L(\lambda_2)}{\partial \lambda_2} d\tau_1 \right. \\
&+ \left. \left[ \int M^L(\mu_1) M^L(\mu_2) L^L(\lambda_2) (\lambda_1^2-\mu_1^2) \frac{1}{r_{12}} [(1-\mu_2^2)(\mu_2-\lambda_1\lambda_2\mu_1) + \mu_2 D(\lambda_1, \lambda_2, \mu_1, \mu_2)] \right] \right. \\
&\quad \left. M^R(\mu_1) L^R(\lambda_1) \frac{\partial M^R}{\partial \mu_2} d\tau_1 \right.
\end{aligned}$$

$$D(\lambda_1, \lambda_2, \mu_1, \mu_2) = (\lambda_1^2 - 1)^{\frac{1}{2}} (1 - \mu_1^2)^{\frac{1}{2}} (\lambda_2^2 - 1)^{\frac{1}{2}} (1 - \mu_2^2)^{\frac{1}{2}} \cos(\phi_1 - \phi_2)$$

$$d\tau_1 = d\lambda_2 d\mu_1 d\mu_2 d\phi_1 d\phi_2 \quad (C6)$$

$$G_1(\mu_1) = \frac{R^5}{32} \left[ \int L^L(\lambda_1) L^L(\lambda_2) M^L(\mu_2) \frac{1}{r_{12}} [(1 - \mu_1^2)(\mu_1 - \mu_2 \lambda_1 \lambda_2) + D(\lambda_1, \lambda_2, \mu_1, \mu_2)] \right.$$

$$\left. \cdot L^R(\lambda_1) L^R(\lambda_2) M^R(\mu_2) d\tau_2 \right] \frac{\partial}{\partial \mu_1} \quad (C7)$$

$$G_2(\mu_1) = \frac{R^5}{32} \left( \int L^L(\lambda_1) L^L(\lambda_2) M^L(\mu_2) \frac{1}{r_{12}} [(\lambda_1^2 - 1)(\lambda_1 - \mu_1 \lambda_2 \mu_2) - \lambda_1 D(\lambda_1, \lambda_2, \mu_1, \mu_2)] \right.$$

$$(\lambda_1^2 - \mu_1^2) \frac{\partial L^R(\lambda_1)}{\partial \lambda_1} L^R(\lambda_2) M^R(\mu_2) d\tau_2$$

$$+ \int L^L(\lambda_1) L^L(\lambda_2) M^L(\mu_2) \frac{1}{r_{12}} [(\lambda_2^2 - 1)(\lambda_2 - \mu_2 \lambda_1 \mu_1) - \lambda_2 D(\lambda_1, \lambda_2, \mu_1, \mu_2)]$$

$$(\lambda_2^2 - \mu_2^2) \frac{\partial L^R(\lambda_2)}{\partial \lambda_2} L^R(\lambda_1) M^R(\mu_2) d\tau_2$$

$$- \int L^L(\lambda_1) L^L(\lambda_2) M^L(\mu_2) \frac{1}{r_{12}} [(1 - \mu_2^2)(\mu_2 - \lambda_1 \lambda_2 \mu_1) + \mu_2 D(\lambda_1, \lambda_2, \mu_1, \mu_2)]$$

$$(\lambda_2^2 - \mu_2^2) L^R(\lambda_1) L^R(\lambda_2) \frac{\partial M^R(\mu_2)}{\partial \mu^2} d\tau_2 \quad (C8)$$

$$d\tau_2 = d\lambda_1 d\lambda_2 d\mu_2 d\phi_1 d\phi_2$$

$F_1^1(\lambda_2)$ ,  $F_2^1(\lambda_2)$ ,  $G_1^1(\mu_2)$ ,  $G_2^1(\mu_2)$  are easily obtained from

(C.7) and (C.8) by using

$$F_{12}^{\dagger} = -F_{12} + \frac{1}{2} \frac{1}{r_{12}} - \left| \frac{\nabla_i e^{\frac{1}{2} r_{12}}}{e^{\frac{1}{2} r_{12}}} \right|^2$$

so interchanging  $L^L$  and  $L^R$   $M^L$  and  $M^R$

$$F_1'(\lambda_1) = -F(\lambda_1) \quad \text{in (C8 - C7)}$$

$$G_1'(\mu_1) = -G(\mu_1)$$

$$F_2'(\lambda_2) = -F_2(\lambda) + \frac{R^5}{32} \int L(\lambda_2)M(\mu_1)M(\mu_2) \frac{1}{r_{12}} (\lambda_1^2 - \mu_1^2) (\lambda_2^2 - \mu_2^2) .$$

$$L(\lambda_2)M(\mu_1)M(\mu_2)d\tau_1$$

$$G_2'(\mu_2) = -G_2(\mu) + \frac{R}{32} \int L^R(\lambda_1)L^R(\lambda_2)M^R(\mu_1)M^R(\mu_2) \frac{1}{r_{12}} (\lambda_1 - \mu_1^2) (\lambda_2^2 - \mu_2^2)$$

$$L^L(\lambda_1)L^L(\lambda_2)M^L(\mu_1)M^L(\mu_2)d\tau_2$$

# APPENDIX D

## ENDPOINT CORRECTIONS

The trapezoidal rule approximations to most integrals occurring in the work described in this thesis require endpoint corrections. For example equation (2.24) should include terms,  $(Y_0^2 (\frac{4\rho_0^2}{4\rho_0^2 - (s^{\frac{1}{2}} - 1)}) + Y_{N2}^2 (\frac{4\rho_{N2}^2}{4\rho_{N2}^2 - (s^{\frac{1}{2}} - 1)})) / 2$  since  $Y_0$  and  $Y_{N2}$  are not necessarily zero. Endpoint corrections must also be included in any coulomb or exchange integrals computed. The way this is done is as follows, expanding  $L(\lambda)$  in a Taylor series about the first mesh point  $\lambda_1$  gives

$$L(0) = L(\lambda_1) + \left. \frac{dL}{d\lambda} \right|_{\lambda_1} (\lambda_0 - \lambda_1) + \frac{1}{2} \left. \frac{d^2 L}{d\lambda^2} \right|_{\lambda_1} (\lambda_0 - \lambda_1)^2 + \dots \quad (D1)$$

By truncating (D1) after the second order term and replacing the derivatives with their finite difference approximations we obtain, after some algebra,

$$\begin{aligned} L(0) = & \frac{(1-ch_1)}{2h_1+(1-2c)h_1^2} X_1 - \frac{h_1}{2h_1+(1-2c)h_1^2} [X_2/2h_1 - \\ & 2 \frac{(1+(1-c)h_1)(1-ch_1)}{2h_1+(1-2c)h_1^2} X_1] + \\ & \frac{1}{2} \frac{h_1^2}{(2h_1+(1-2c)h_1^2)(1-ch_1)} [(X_2-2X_1)/h_1^2 - 4 \frac{(1+(1-c)h_1)(1-ch_1)}{2h_1+(1-2c)h_1^2} X_2/2h_1 \\ & + \frac{(1-ch_1)^2}{(2h_1+(1-2c)h_1^2)} \cdot (4 + (6-7c)h_1 + (1+c)ch_1^2 X_1] \quad (D2) \end{aligned}$$

Note that the correction is expressed in terms of the finite difference variables  $X_k$ . Endpoint corrections for all the other integrals are obtained in a similar manner.

There is one further difficulty associated with numerical integration. It occurs when the von Neumann expansion (B3) of  $\frac{1}{r_{12}}$  occurs in the integrand. Consider the integral  $\int_1^\infty L_1^2(\lambda_1) L_2^2(\lambda_2) \frac{1}{r_{12}} d\lambda_1 d\lambda_2$  when  $\frac{1}{r_{12}}$  is expanded using (B3) the  $Q_k^{(m)}(\lambda_>)$  term causes a singularity at  $\lambda=1$  when  $L_1(1)$  and  $L_2(1)$  are nonzero. The integral still converges but the trapezoidal rule approximation does not. This problem is overcome by representing the  $\lambda$  wavefunctions by Taylor expansion (D1) and integrating between the zeroth and first mesh point analytically.

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